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The Crystal Structure of Cesium Enneachlordithalliate, $Cs_3Tl_2Cl_9$

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$Cs_3Tl_2Cl_9$ is shown to possess a rhombohedral unit of structure with $a_0=9.58$A, $\alpha=83°\ 48'$, containing two molecules. The crystals exhibit extensive and quite perfect 60° twinning on the basal plane, so that most specimens simulate complete sixfold symmetry, but when this is taken into consideration, a structure based upon $D_{3d}^6-R\,\bar{3}\,c$ accounts well for observed intensity data. The structure may be described conveniently as an aggregate of Cs^+ and $Tl_2Cl_9^{-3}$ groups packed together in such manner that all large atoms fit into an approximately closest-packed arrangement. The $Tl_2Cl_9^{-3}$ group is considered to be a covalent complex. The derived structure is compared with the known structures of $Cs_3As_2Cl_9$ and $KMgF_3$.

INTRODUCTION

IN the course of a search for compounds of trivalent thallium which would lend themselves to structural investigations, we have examined cesium enneachlordithalliate, $Cs_3Tl_2Cl_9$, first prepared by Pratt.[1] While this compound can scarcely be considered remarkable for the simplicity of its structure, it has proved more amenable to treatment than other thallic salts, which seem in general to crystallize with highly complex structures. We have determined from x-ray data the atomic arrangement existing within crystals of $Cs_3Tl_2Cl_9$, leading to some interesting results with regard to the coordination and bonding properties of Tl^{III} in addition to accounting for the stability of crystals of this formula.

DETERMINATION OF THE STRUCTURE

In accordance with the results of Pratt, we were able to prepare clear stable crystals of $Cs_3Tl_2Cl_9$ with two different habits: Very thin uniaxial hexagonal plates and hexagonal prisms, depending upon the relative concentrations of CsCl and $TlCl_3$ in the solutions from which the compound crystallized. The compound is highly absorbing, but as the plates were less than 0.1 mm in thickness, it was possible to get x-ray data from various types of transmission photographs. We have for the most part worked with the plates, although such data as were obtained for the prisms are in agreement with the derived structure.

Most of our Laue photographs, prepared with the incident beam exactly perpendicular to the basal plane, show no deviation from the symmetry of D_{6h}. In two cases, however, we found exceedingly thin crystals which gave excellent Laue photographs showing only the symmetry of D_{3d}. With either type of crystal the smallest hexagonal unit which accounts for the numerous data of our Laue and oscillation photographs is one with $a_0=12.8$A, $c_0=18.30$A. Our value of the axial ratio, $c_0/a_0=1.43$, agrees within the limit of error with the crystallographic value, $\sqrt{3}\cdot 0.8257=1.430$.

That we have to deal with extensive and quite

[1] Pratt, Am. J. Sci. **149**, 397 (1895). See also Groth, Chem. Kryst. Engelmann, Leipzig **1**, 437 (1908).

perfect twinning on the basal plane is rendered highly probable by the following considerations: We find that the sixfold symmetry of the one type of photograph can be completely reproduced both as to the positions and relative intensities of all spots by the simple process of superposition of two of the threefold patterns after one of them has been rotated through 60° about c. We simply average the intensities of $\{HI\cdot L\}$ and $\{HI\cdot\bar{L}\}$ of the threefold pattern to get the corresponding intensities of either form in the sixfold pattern.

All of the data of the threefold photographs, moreover, are accounted for by the rhombohedral unit with one-third the volume of the hexagonal unit. This unit, which has $a_0=9.58\pm0.04$A, $\alpha=83°\,48'\pm15'$, contains 2 $Cs_3Tl_2Cl_9$ and leads to a calculated density of 4.32 g/cc, is to be accepted as the true one.

The regular vanishings[2] observed are $\{hhl\}$ with l odd. The space-groups accounting for these are $C_{3v}{}^6-R\,3\,c$ and $D_{3d}{}^6-R\,\bar{3}\,c$.

The crystal radius[3] for coordination number six of Cl^- is 1.81A. A hexagonal unit of 6 layers made up of 72 spheres of this size in closest-packing would have $a_0=12.54$A, $c_0=17.72$A. Our hexagonal cell contains 54 Cl^- and 18 Cs^+, the latter with radius 1.69A only slightly smaller than that of Cl^-. As we find $a_0=12.8$A, $c_0=18.3$A, it appears highly probable that cesium and chlorine ions are to be found in a nearly closest-packed arrangement in $Cs_3Tl_2Cl_9$. Remembering that within this hexagonal cell we must have the rhombohedral lattice points at $\frac{2}{3}\frac{1}{3}\frac{1}{3}$ and $\frac{1}{3}\frac{2}{3}\frac{2}{3}$, and adding the quite reasonable assumption that two cesium ions are not to be in contact with each other, we are led to a unique distribution (excepting small distortions) of the 18 Cs^+ and 54 Cl^- within the hexagonal cell. We may conveniently symbolize this ideal arrangement, which is made up of identical layers, as follows: Let A represent a closest-packed layer containing 3 Cs and 9 Cl with Cs at $0\frac{2}{3}$, $\frac{1}{3}\frac{1}{3}$, $\frac{2}{3}0$, B a similar layer with Cs at $0\frac{1}{3}$, $\frac{2}{3}\frac{2}{3}$, $\frac{1}{3}0$. The sequence of layers along c is then $ABABAB\cdots$, corresponding to hexagonal closest-packing (see Fig. 1).

If thallium and cesium atoms are not to be in contact, and the resulting structure is to possess rhombohedral symmetry, the 12 Tl are to be placed in approximate positions given by $Z\doteqdot\pm1/12$ and $\pm5/12$ relative to each rhombohedral lattice point. Each Tl is then surrounded by 6 Cl. This undistorted or ideal structure can be developed from either $C_{3v}{}^6$ or $D_{3d}{}^6$, in both cases with highly specialized parameter values. A careful study of the structure reveals no reason for eliminating the centers of symmetry and twofold axes, and we accordingly assume $D_{3d}{}^6$ to be the correct space-group.

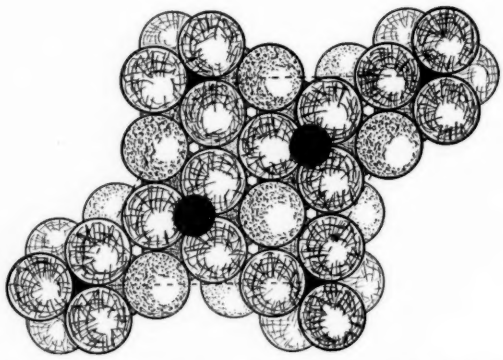

FIG. 1. Packing drawing of two layers parallel to (00·1) showing the undistorted closest-packed structure. Cesium may be distinguished from chlorine atoms by the type of shading.

Using the rhombohedral notation of Wyckoff[4] proper to $D_{3d}{}^6$, we have the following assignment of positions: 4 Tl in $4c$, uuu, *etc.* 6 Cs in $6e$, $v\bar{v}o$, *etc.* 6 Cl in $6e$, $w\bar{w}o$, *etc.* 12 Cl in $12f$, xyz, *etc.* We expect $u\geqslant1/12$, $v\doteqdot\frac{2}{3}$, $w\leqslant\frac{1}{6}$, $x\doteqdot\frac{1}{3}$, $y\doteqdot\frac{1}{6}$, $z\doteqdot0$.

The basal plane reflections deserve special consideration since they involve but two parameters. Only the even orders appear of course, for which

$$S_{(nnn)}=4f_{\mathrm{Tl}}\cos 6\pi nu+6(f_{\mathrm{Cs}}+f_{\mathrm{Cl}})+12f_{\mathrm{Cl}}\cos 2\pi n(x+y+z).$$

Intensities were calculated from the formula

$$I=C\frac{1+\cos^2 2\theta}{2\sin 2\theta}n|S|^2.$$

The f-values of Pauling and Sherman[5] are used

[2] Astbury and Yardley, *Tabulated Data for the Examination of the 230 Space-Groups by Homogeneous X-Rays*, Phil. Trans. **224**, 221 (1924).

[3] Linus Pauling, J. Am. Chem. Soc. **49**, 765 (1927).

[4] R. W. G. Wyckoff, *The Analytical Expression of the Results of the Theory of Space-Groups*, 2nd Ed., p. 157. Carnegie Institution of Washington, 1930.

[5] Pauling and Sherman, Zeits. f. Krist. **81**, 1 (1932).

throughout this paper. No temperature factor is included. The extremely thin plate-like but very strongly absorbing crystals used for these photographs were so small as always to be completely bathed in radiation; the effective cross section taken from the beam was proportional therefore to sin θ, or to n.

A comparison of calculated with observed intensities for the first four orders from (111) with $u=0.098$, $x+y+z=\frac{1}{2}$ (the value for undistorted closest-packing) is given in Table I.

TABLE I. *Comparison of calculated with observed intensities for (nnn) reflections.* $u=0.098$, $x+y+z=\frac{1}{2}$.

n	Observed intensity	Calculated intensity*
2	16	16
4	24	29
6	8	18
8	1	4

* Temperature factor not included.

The agreement is quite satisfactory, but is seriously impaired if the value of u be changed by more than about 0.002. A small deviation of the chlorine parameter ($x+y+z=3Z$, where Z is the parameter along the hexagonal axis) from the ideal value $\frac{1}{2}$ is to be expected, although exerting a nearly inappreciable effect upon the calculated intensities.

Table II contains a comparison of calculated with observed intensities for a group of reflections which do not depend upon the thallium parameter using the closest-packed values for cesium and chlorine. The technique here employed was that of transmission through a thin plate which was completely bathed in radiation, and the formula used in calculation was similar in form to that for (*nnn*) reflections except for the omission of the factor n. The intensity comparisons of Table II provide strong evidence that we have arrived at essentially the correct structural type, although small deviations from the ideal parameter values are probably indicated. A change of ± 0.01–0.02 from the value $\frac{2}{3}$ of the cesium parameter, which affects the calculated intensities quite appreciably, is certainly dimensionally admissible. A change in either direction decreases somewhat the calculated intensities of all the reflections with appreciable structure factors of Table II excepting the last three, which are increased. We have not been able to decide in which direction the parameter value should be moved, so that we are giving interatomic distances in Table III for $v=\frac{2}{3}$.

TABLE II. *Comparison of calculated with observed intensities for reflections independent of* u. $v=\frac{2}{3}$, $x=\frac{1}{3}$, $y=\frac{1}{6}$, $z=0$, $w=\frac{1}{6}$.

(*hkl*)	*Intensity* Obs.	Calc.*	(*hkl*)	*Intensity* Obs.	Calc.*
$10\bar{1}$	24	24	$6\bar{3}\bar{3}$	5	9.7
$20\bar{2}$	0	0.04	$8\bar{4}\bar{4}$	3	13.
$30\bar{3}$	16	32	$10,\bar{5},\bar{5}$	0	2.5
$40\bar{4}$	0	0.09	$41\bar{5}$	4	10
$50\bar{5}$	<1	1.5	$52\bar{7}$	1.5	4.8
$60\bar{6}$	6	18	$21\bar{3}$	5	5.6
$21\bar{1}$	48	67	$32\bar{5}$	1	1.2
$42\bar{2}$	36	54	$31\bar{4}$	2	2.5

* Temperature factor not included.

TABLE III. *Interatomic distances in* $Cs_3Tl_2Cl_9$.

Atom	Neighbors	Separation	Atom	Neighbors	Separation
Tl	3 Cl_I	2.66A	Cl_I	2 Cl_I	3.39A
Tl	3 Cl_{II}	2.54	Cl_I	2 Cl_{II}	3.77
Cs	2 Cl_I	3.70	Cl_I	2 Cl_{II}	3.75
Cs	2 Cl_I	3.83	Cl_I	2 Cl_{II}	3.80
Cs	2 Cl_{II}	3.76	Cl_{II}	2 Cl_{II}	3.78
Cs	2 Cl_{II}	3.62	Cl_{II}	2 Cl_{II}	3.68
Cs	4 Cl_{II}	3.74	Cl_{II}	1 Cl_{II}	3.68

The intensity data of Tables I and II were obtained from twinned crystals, but include only planes which possess structure factors independent of the type of twinning postulated.

Discussion of the Structure

A diagram illustrating the closest-packing of the cesium and chlorine atoms of two layers is shown in Fig. 1. Disregarding the thallium atoms, which are introduced in positions of rhombohedral symmetry, the fundamental translation along c of the closest-packed arrangement is just the thickness of two layers. As placed in the derived structure each Tl is surrounded by 6 Cl, but pairs of $TlCl_6$ octahedra share faces to give Tl_2Cl_9 groups. In the two molecule rhombohedral unit, we find a Tl_2Cl_9 group of symmetry D_3 at the origin and an equivalent group at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. These groups fit together along the threefold axes to form closest-packed columns, which are bound together by cesium ions in such manner as

to complete the closest-packing in three dimensions.

The radius ratio of the univalent radii,[6] $r_{Tl^{+3}}/r_{Cl^-}=0.635$, indicates that thallic thallium should show a coordination number of six (or perhaps more) toward chloride ion if the ionic model be a good approximation. The mere existence in this structure of the complex Tl_2Cl_9 groups, in which $TlCl_6$ octahedra share faces, is enough to show that the ionic model is unsatisfactory. It seems very improbable that a solution containing a mixture of truly ionic Tl^{3+}, Cl^- and Cs^+ (or ionic complexes) would give rise to crystals in which the thallium atoms are placed so near together in pairs, although crystals of this composition have actually a rather wide range of stability. We conclude therefore that the Tl_2Cl_9 ion is essentially a covalent complex, and we find that an assignment of parameter values for chlorine differing but little from the ideal set together with the experimentally determined value for the thallium parameter give rise to interatomic distances in agreement with this view. With $x=0.336$, $y=0.176$, $z=-0.005$ and $w=0.153$, we find $Tl-Cl_I=2.66$A, $Tl-Cl_{II}=2.54$A and the Cl−Cl separations given in Table III. These Tl−Cl separations may be compared with the sum of the ionic radii,[7] 2.76A, and the covalent bond distance, 2.55A, obtained by adding the "octahedral" radius[8] of Tl^{III} to the covalent radius of chlorine (for which the "tetrahedral" and "normal" radii are equal). Because of the mutual repulsions of the (somewhat ionic) thallium atoms within the complex and to the less favorable bond angle, 79° 20′ as against 96° 20′, the Tl−Cl bonds involving the shared chlorine atoms are somewhat weaker than the others. The value of w is assumed so as to make the shared face of the complex have somewhat shortened edges, in analogy to what is observed in truly ionic crystals. A change in this value of w together with a possible small change from the value of the thallium parameter as determined would modify slightly the bond angle and interatomic distance for $Tl-Cl_I$.

The structure of $Cs_3Tl_2Cl_9$ is related to the structures of $Cs_3As_2Cl_9$[9] and $KMgF_3$ by virtue of the fact that all of them are based upon closest-packing of the large cations and anions, which occur in the ratio one to three. Characteristic molecular aggregates are, however, very different within the three structures, for we find, respectively, $Tl_2Cl_9^{-3}$, $AsCl_3$ and MgF_6^{-4} occurring as rather well-defined groups.

We are indebted to Professor Linus Pauling for invaluable suggestions during the course of this work.

[6] Linus Pauling, J. Am. Chem. Soc. **49**, 765 (1927). Ibid. **51**, 1010 (1929).
[7] Linus Pauling, J. Am. Chem. Soc. **49**, 765 (1927).
[8] Pauling and Huggins, Zeits. f. Krist. **87**, 205 (1934).
[9] Hoard and Goldstein, J. Chem. Phys. **3**, 117 (1935).

The Crystal Structure of Diaspore*

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The parameters in diaspore are redetermined, and the structure is discussed from the standpoint of the coordination theory. The existence and location of hydrogen bonds in the structure are established, and representative formulas are proposed.

INTRODUCTION

THE mineral diaspore, $AlHO_2$, is described as forming orthorhombic crystals, with the axial ratios $a:b:c=0.9372:1:0.6039$, according to Groth. Its composition, symmetry and axial ratios suggest its isomorphism with the goethite modification of $FeHO_2$, and with manganite, $MnHO_2$. A second modification of $FeHO_2$, lepidocrocite, also exists and forms orthorhombic crystals. The existence of a second modification of $AlHO_2$ corresponding to lepidocrocite is indicated by the x-ray studies made by Böhm[1] on certain bauxites.

Work begun by the writer in 1929 had disclosed the structure of diaspore and suggested a probable structure for lepidocrocite. The completion of this work was unavoidably delayed until recently, and in the meantime the structure of diaspore was derived by Deflandre[2] and independently by Takané,[3] and Goldsztaub[4] found that the goethite structure was essentially that of diaspore.

In the present paper the diaspore-goethite structure is discussed from the standpoint of the coordination theory, with particular reference to the distribution of the hydrogen atoms and their relation to the existence of a second modification.[5] The results of a more accurate determination of the parameters in diaspore are given, and the interatomic distances thus determined are shown to establish the existence and location of the hydrogen bonds as suggested by the coordination theory.

THE UNIT OF STRUCTURE, SPACE GROUP SYMMETRY AND THE GENERAL POSITIONS OF THE ATOMS

The unit cell of diaspore was determined from oscillation and Laue photographs to correspond to the axial lengths

$$a=4.40\text{A}, \qquad b=9.39\text{A}, \qquad c=2.84\text{A}.$$

These values give the axial ratios $0.469:1:0.302$, in good agreement with the crystallographic ratios $0.4686:1:0.3020$ obtained by doubling the b-axis. The observed density of diaspore, 3.4, indicates that a unit of these dimensions contains $4\ AlHO_2$.

The space group of diaspore was determined from Laue data to be $V_h^{16}-Pbnm$, as found by Deflandre and Takané.

The observed even orders of reflection from (001) were found to decline normally in intensity, indicating that all the atoms are situated in planes perpendicular to c at a distance $c/2$ apart. To place the oxygens anywhere except on the reflection plane m would give O−O distances of 1.42A or less, which is impossible. All the atoms therefore lie on the m reflection planes, the general positions, referred to a center of symmetry as origin, being as follows:

$4\ \text{Al at } u,v,-\frac{1}{4};\frac{1}{2}-u,\frac{1}{2}+v,-\frac{1}{4};\frac{1}{2}+u,\frac{1}{2}-v,\frac{1}{4};\bar{u},\bar{v},\frac{1}{4}.$
$4\ O_I \text{ at } u_1,v_1,-\frac{1}{4};\text{etc.}$
$4\ O_{II} \text{ at } u_2,v_2,-\frac{1}{4};\text{etc.}$

THE DETERMINATION OF PARAMETERS

Oscillation photographs were taken of Mo $K\alpha$ radiation by reflection from (010), ten even orders of reflection being observed. Using the usual methods it was found that the observed intensities of reflections at large angles serve to fix v, the aluminum parameter, at $+0.144\pm0.003$ irrespective of the oxygen positions. By using

* No. 456.
[1] J. Böhm, Zeits. f. anorg. Chemie **149**, 203 (1925).
[2] M. Deflandre, Bull. Soc. Franc. Mineral. **55**, 140 (1932).
[3] Takané, Proc. Imp. Acad. Tokyo **9**, 113 (1933).
[4] S. Goldsztaub, Comptes rendus **195**, 964 (1932).
[5] The structure of the second modification as typified by lepidocrocite will be described in a future publication.

values of the aluminum parameter within these limits it was then found possible on the basis of observed intensities to fix the oxygen parameters within the ranges $-0.216<v_1<-0.190$ and $-0.062<v_2<-0.042$. The parameters were then adjusted within these limits to give the best quantitative relation between observed and calculated intensities. The values thus obtained are

$$v=+0.146\pm0.001, \qquad v_1=-0.200\pm0.002,$$

and $$v_2=-0.052\pm0.002,$$

in which the probable limits of error as given correspond to the minimum displacement causing disagreement between observed and calculated intensities. The extent of the agreement between observed and calculated intensities of reflection from (010) using these values of the parameters is shown in Table I.

TABLE I. *Observed and calculated intensities of reflection on oscillation photograph from* (010) *with* [001] *as axis.*

{*hkl*}	*Intensity* Obs.[a]	Calc.[b]	{*hkl*}	*Intensity* Obs.[a]	Calc.[b]
(020)	4.0	5.4	(021)	2.0	1.7
(040)	10	7.3	(041)	4.5	4.0
(060)	6.0	4.7	(061)	25	17.5
(080)	0.25	1.2	(081)	4.0	3.0
(0.10.0)	3.0	2.1	(0.10.1)	0.7	0.15
(0.12.0)	0.7	0.15	(0.12.1)	1.4	0.79
(0.14.0)	1.1	0.48	(0.14.1)	0.85	0.22
(0.16.0)	0.0	0.03	(0.16.1)	0.5	0.16
(0.18.0)	0.25	0.07	(0.18.1)	0.0	0.04
(0.20.0)	0.7	0.15	(0.20.1)	0.0	0.03

[a] Estimated visually, and corrected in the case of side spectra for varying time of reflection.
[b] Based on Bragg and West's *f* values.

The relative shortness of the *a*-axis limits the amount of diffraction data obtainable by reflection from (100), so that an exact determination of the parameters along *a* by rigorous methods is difficult. By assumptions which will be discussed in the next section it is possible to predict values of these parameters, the predicted values being

$$u=-0.036, \qquad u_1=+0.27, \qquad u_2=-0.21.$$

These values give excellent quantitative agreement between the calculated and observed intensities of reflection, as is shown in Table II. A shift of 0.01 in any of these parameters somewhat impairs the quantitative nature of the agreement.

TABLE II. *Observed and calculated intensities of reflection on oscillation photograph from* (100) *with* [001] *vertical.*

{*hkl*}	Intensity Obs.[a]	Calc.[b]	{*hkl*}	Intensity Obs.[a]	Calc.[b]
(200)	0.2	0.13	(101)	0.8	0.81
(400)	5.0	3.4	(301)	1.7	2.2
(600)	0.0	0.00	(501)	0.5	0.57
(500)	0.0	0.08	(701)	0.3	0.28

[a] Estimated visually, and corrected in the case of side spectra for varying time of reflection.
[b] Based on Bragg and West's *f* values.

The parameter values determined by Deflandre are, restated in our convention, $u=-0.042$, $u_1=+0.25$, $u_2=-0.25$, $v=+0.144$, $v_1=-0.20$, $v_2=-0.05$. His values for v, v_1 and v_2 are in close accord with ours, but his values for u, u_1 and u_2 do not account quantitatively for reflections from (100) as well as do ours. This is illustrated, for instance, by the reflection (701), which is observed 0.6 as strong as (501); the calculated ratio is 0.5 using our parameters values and 0.2 using Deflandre's values. Takané's parameter values differ more widely from ours, and lead in some instances to calculated intensities that are in qualitative disagreement with our data.

DISCUSSION OF THE STRUCTURE

The diaspore-goethite structure can be regarded as built of aluminum or iron centered octahedra arranged in the manner shown in Fig. 1. The octahedra share edges in such a way as to form one-dimensionally infinite aggregates which may be called "double rutile strings" running parallel to the *c* axis. These strings are joined by sharing corners, as shown in the figure. Each anion is common to three octahedra.

This type of structure is readily predictable on the basis of the coordination theory[6] if a distribution of the hydrogens is assumed giving all the anions the form $(OH_1)^{-\frac{1}{3}}$, such anions being required by the electrostatic valence rule to be shared between three octahedra.[7] The only alternative distribution of the hydrogens gives the anions $O^{=}$ and OH^{-}, and the electrostatic

[6] Linus Pauling, J. Am. Chem. Soc. **51**, 1010 (1929).
[7] With the character of the polyhedra and their method of sharing defined, the number of structures fitting the unit cell is greatly limited, and the structure shown in Fig. 1 is the only one that is immediately apparent under the conditions given.

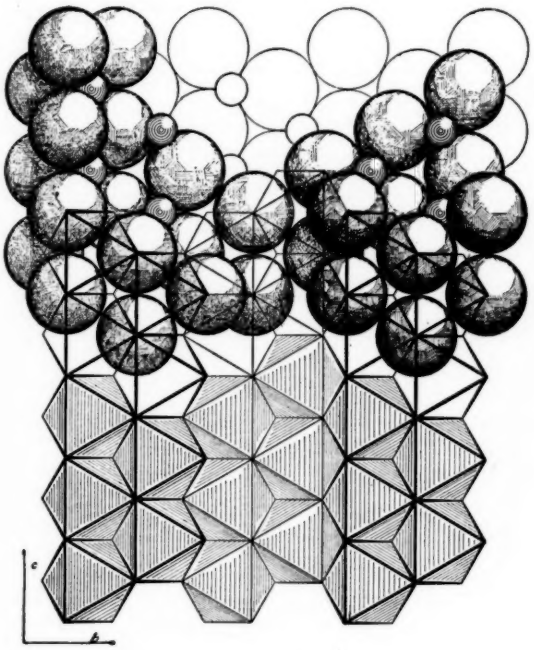

FIG. 1. The ideal structure of diaspore, showing the "double rutile strings" formed by the aluminum-centered oxygen octahedra. The relationship between the octahedra and the close packed arrangement of the oxygens is also shown. The aluminums are represented by the small spheres.

valence rule requires that $O^=$ and OH^- anions be shared between four and two octahedra, respectively. This latter type of sharing is actually that found in the structure of the second modification of $FeHO_2$, lepidocrocite.[5]

The coordination theory not only gives the ideal structure successfully, but also indicates the degree of distortion to be expected. Edges shared between octahedra, according to the rule for distortion, should be reduced to 2.50A, with other edges being compensatorily lengthened. The lengthened edge is given in the case of diaspore by the c identity distance, 2.84A. By fitting the distorted octahedra to the unit cell values for the entire set of parameters can be obtained, and v, v_1 and v_2 thus obtained are within 0.02 of the values derived rigorously from intensity measurements.

Starting with the rigorously determined values of v_1 and v_2 the requirement that shared edges be 2.50A long leads directly to the values of $+0.27$ and -0.21 for u_1 and u_2, respectively. As previously shown arguments based on quantitative agreement with intensities serve to confirm these values, but equally important is the fact that they introduce into the structure the 2.50A shared edge which appears in many accurately known structures such as rutile, anatase, brookite, and corundum, and which has been shown to correspond to a minimum of crystal energy in the case of rutile and anatase.[8]

The value of -0.036 for the aluminum parameter u is calculated by making the reasonable assumption that structurally similar Al$-$O distances inside the octahedron are equal, i.e. that the aluminum is equidistant from the three oxygens in the center of the double rutile string, and likewise equidistant from the three oxygens at the corner of the string. These two conditions lead to slightly different values for u, the average of which is given by -0.036.

The formal existence of $(OH_1)^{-\frac{1}{2}}$ anions is most readily explained by postulating hydrogen bonds between pairs of oxygens. Hydrogen bonds, forming collinear OHO groups, have been found in certain crystals containing oxygen and acidic hydrogen, namely H_3BO_3,[9] $NaHCO_3$,[10] and K_2HPO_4,[11] and in ice[12] and the crystalline hydrates $H_2C_2O_4\cdot 2H_2O$ [13] and $Li_2SO_4\cdot H_2O$.[14] The hydrogen bond has also been shown to exist in gaseous $(HCOOH)_2$ by means of electron diffraction methods.[15]

In diaspore the location of the hydrogen bonds can be expected to be between oxygens in different octahedra because of the effect of Al$-$H repulsion; their exact location is finally determined by a comparison of the interatomic distances concerned.

Interatomic distances calculated from our values of the parameters are shown in Table III. With the exception of the shared edges (which are 2.50A long), the O$-$O distances within each octahedron lie in the range from 2.73 to 2.84A, or somewhat in excess of 2.70A, the sum of the ionic radii. Between different octahedra the O$-$O distances are 3.10A or greater with the important

[8] Linus Pauling, Zeits. f. Krist. **67**, 377 (1928).
[9] W. H. Zachariasen, Zeits. f. Krist. **88**, 150 (1934).
[10] W. H. Zachariasen, J. Chem. Phys. **1**, 634 (1933).
[11] J. West, Zeits. f. Krist. **74**, 306 (1930).
[12] W. H. Barnes, Proc. Roy. Soc. (London) **125**, 670 (1929).
[13] W. H. Zachariasen, Zeits. f. Krist. **89**, 442 (1934).
[14] G. E. Ziegler, Zeits. f. Krist. **89**, 456 (1934).
[15] L. Pauling and L. O. Brockway, Proc. Nat. Acad. Sci. **20**, 336 (1934).

TABLE III. *Interatomic distances in diaspore.*

Atom	Neighbors in same octahedron	Neighbors in other octahedra
O_I	2 O_I at 2.84A 4 O_I at 2.78 2 O_{II} at 2.78 2 O_{II} at 2.73 1 O_{II} at 2.50	2 O_{II} at 4.11A 2 O_{II} at 3.92 1 O_{II} at 2.71
O_{II}	2 O_{II} at 2.84A 2 O_I at 2.78 2 O_I at 2.73 2 O_{II} at 2.50 1 O_I at 2.50	2 O_I at 4.11A 2 O_I at 3.92 2 O_{II} at 3.10 1 O_I at 2.71
Al	1 O_{II} at 2.01A 2 O_{II} at 1.98 1 O_I at 1.86 2 O_I at 1.82	2 Al at 3.10A

exception of the 2.71A distance. This distance of 2.71A is not only characterized by the fact that it is much the shortest of similar distances, but also by the fact that it is inexplicably so unless it is assumed to correspond with a hydrogen bond.

The location of the 2.71A distances in the diaspore structure is shown by the small tubes in Fig. 2. This figure perhaps makes it clear that by slightly twisting the double strings about their points of contact the distances corresponding to the tubes can be lengthened and brought into equality with other O−O distances between octahedra. The only apparent explanation for the structure having a twist which differentiates these distances is that the tubes correspond to hydrogen bonds.[16]

The allocation of one hydrogen to each tube gives the correct stoichiometric composition to the crystal, and hence accounts for all of the hydrogens.

The value of 2.71A found for the OHO distance in diaspore is in agreement with the values 2.71 and 2.67A found in H_3BO_3 and $(HCOOH)_2$, respectively, and lies somewhat above the values 2.54 and 2.55A found in K_2HPO_4 and $NaHCO_3$, and below the values 2.77 and 2.96A found in H_2O and $Li_2SO_4 \cdot H_2O$. This indicates that the strength of the hydrogen bond in diaspore is considerably greater than that in ice or in the hydrate $Li_2SO_4 \cdot H_2O$, and is approximately the same as in H_3BO_3 and $(HCOOH)_2$.

The Al−O distances in diaspore correspond closely to the Al−O distances of 1.99 and 1.85A found in corundum, since in diaspore the Al−O_{II} distances average 1.99A and the Al−O_I distances average 1.84A. The slight deviations of 0.01 to 0.02A from these average Al−O distances shown in Table III are within the error of the parameter determinations, but on the other hand they are in the proper direction to be related to a distortion produced by the hydrogen bond. In

[16] This differentiation of distances is not seriously affected by variation of the parameter values over ranges considerably greater than their probable error. Deflandre's values of the parameters might have been used to deduce the hydrogen bond, obtaining an OHO distance of 2.60A in comparison with a next smallest distance of 2.80A.

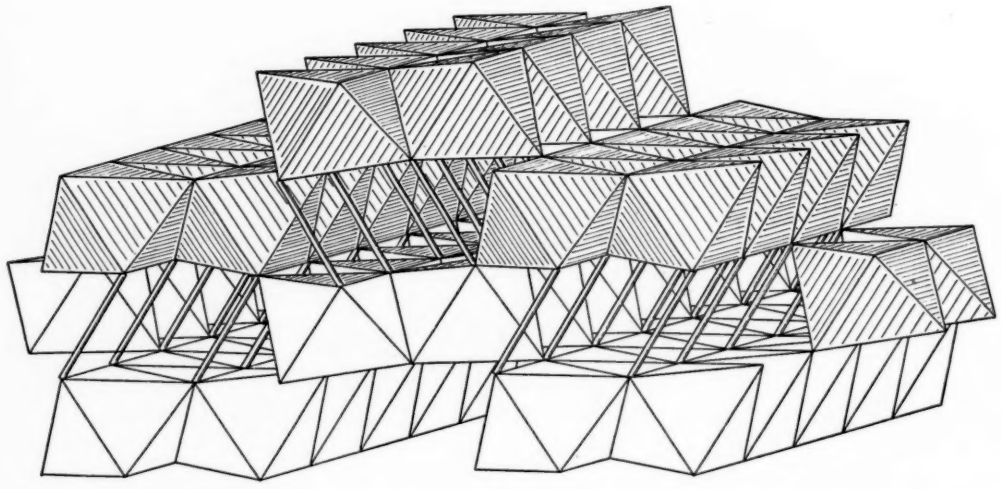

FIG. 2. A pictorial representation of the diaspore structure, with the hydrogen bonds shown as tubes.

both corundum and diaspore the shift of the Al−O distances from 1.90A, the sum of the radii concerned, is evidence of the effect of Al−Al repulsion.

The formula for diaspore we have written $AlHO_2$, the HO_2 group so indicated being taken as representing hydrogen-bonded oxygens. The formula $HAlO_2$ would be equally correct as indicating that both H and Al cations formed coordinated structures with the oxygen cations, and the chemical inference in this latter formula that diaspore is meta-aluminic acid is borne out by the existence of meta-aluminate salts such as the spinels. Either formula would be more correctly written in the polymerized form $(AlHO_2)_n$ or $(HAlO_2)_n$ to admit the known coordination number of 6 for Al. The usual formulas for diaspore, $Al_2O_3 \cdot H_2O$, $Al_2O_2(OH)_2$, or AlO(OH) are wrong in indicating a distinct existence of water or OH^- ions.

I am gratefully indebted to Professor Linus Pauling for his original suggestion as to the probable structure of diaspore and for his interest and advice during the work.

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On the Normal Vibration Frequencies of NH_3, PH_3 and AsH_3

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It is shown that the assumption of valence forces for NH_3, PH_3 and AsH_3 leads to the conclusion that the high frequency, degenerate normal vibration, although theoretically active, does not appear as a fundamental in the infrared spectra of these compounds. This conclusion follows from the fact that the remaining three fundamentals, all of which have been observed, can be accounted for satisfactorily with proper values of the two constants of the potential function for valence forces. The values calculated for this absent frequency with the same force-constants are 3450 cm^{-1}, 2340 cm^{-1} and 2125 cm^{-1} for NH_3, PH_3 and AsH_3, respectively. The frequency for NH_3 may be fixed more precisely at 3470 cm^{-1} if we interpret the 4417 cm^{-1} band as a combination band involving this frequency and the 950 cm^{-1} frequency. Other evidence is given in support of a value for the frequency in the neighborhood of 3450 cm^{-1}. There is, however, the difficulty of explaining why the predicted frequencies are not observed. The 4417 cm^{-1} band is probably to be ascribed to the fourth fundamental in case this fundamental does actually appear. If this is the case, then there is an extreme departure from valence forces in NH_3 and probably likewise in PH_3 and AsH_3. Frequencies are computed for NH_2D, ND_2H and ND_3 to provide a means of testing the value predicted upon the assumption of valence forces for the fourth fundamental in NH_3.

THE justification for using the concept of valence forces in treating NH_3 is based upon its reasonably successful application to H_2O and CH_4. J. H. Van Vleck and P. C. Cross[1] have shown that the fundamental frequencies of H_2O can be computed with fair accuracy using a valence-type potential function. Jenny E. Rosenthal[2] has found that the frequencies of CH_4 are consistent with such a potential function to within six percent. It is therefore justifiable to make the assumption that a similar kind of forces exists in NH_3 and that the valence-type potential function is probably a good first approximation to the general quadratic expression. Any large deviation from this approximation would, on this assumption, then be considered a consequence of the anharmonic terms introduced by the passing of the nitrogen atom through the plane of the hydrogen atoms. Consequently, to afford a comparison with the results obtained for NH_3, we have also considered PH_3 and AsH_3, in which the bonds are doubtless similar to those of NH_3 and in which this so-called tunnel effect is thought to be of less consequence.[3]

[1] J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

[2] Jenny E. Rosenthal, Phys. Rev. **46**, 730 (1934).

[3] See for example D. M. Yost and T. F. Anderson, J. Chem. Phys. **2**, 624 (1934).

Calculation of Frequencies

Under the assumption of valence forces the potential function of the symmetrical pyramidal molecule YX_3 is

$$V=1/2K(\Delta R_1^2+\Delta R_2^2+\Delta R_3^2) +1/2HR_0^2(\Delta\alpha_{12}^2+\Delta\alpha_{23}^2+\Delta\alpha_{31}^2).$$

Here K and H are force constants, ΔR_i is the departure of the distance Y–X_i from its equilibrium value R_0 and $\Delta\alpha_{ij}$ is the departure of the angle X_i–Y–X_j from its equilibrium value α_0. This molecule has four distinct frequencies: ν_1 and ν_3, in the notation of Dennison,[4] denote the high and low frequencies, respectively, of vibrations with change of electric moment parallel to the figure axis. Likewise ν_2 and ν_4 correspond to the high and low frequency vibrations, respectively, with change of electric moment perpendicular to this axis, the latter vibrations being doubly degenerate. All four frequencies are theoretically active in both the Raman and infrared spectra.

Formulas for calculating the fundamental frequencies of vibration have been derived by Lechner[5] and others for the above potential function. In Table I are given the values of K and H which make the calculated values of ν_1 and ν_4 agree with the experimental values we have assigned to these frequencies. The values computed for ν_2 and ν_3 with these force constants are likewise given; in the case of NH_3 this calculated value of ν_3 is the unstarred frequency. It is seen that the difference between the calculated value of ν_3 and the observed frequency in its neighborhood, which we have assigned to ν_3, is rather large for NH_3 but is smaller for PH_3 and AsH_3.

The large discrepancy in the case of NH_3 can be explained as a consequence of anharmonic terms in the potential function and does not otherwise, invalidate the assumption of valence forces. These terms principally affect the ν_3 (950) frequency and necessitate a large correction in obtaining the observed frequency, which corresponds to a vibration with finite amplitude, from the frequency for infinitesimal amplitude of vibration, called the mechanical frequency. Mr. M. F. Manning has kindly consented to calculate the mechanical frequency directly from his symmetric double-minima potential function[8] for NH_3. He finds it to be 1050 cm^{-1}, in contrast to the experimental frequency of 950 cm^{-1}. The value 1110 cm^{-1}, calculated for ν_3 upon the assumption of valence forces, does not, of course, allow for the anharmonic correction. It will resemble the mechanical frequency since the anharmonic corrections for the other frequencies are no doubt much smaller than that for ν_3. Applying Manning's correction to the computed value of ν_3 we obtain a final calculated frequency of 1010 cm^{-1}, which is to be compared with the experimental frequency, 950 cm^{-1}. Thus the agreement between the observed frequency ν_3 and the frequency calculated upon the basis of valence forces is as good for NH_3 as for PH_3 and AsH_3, in which there is probably no large anharmonic correction necessary. Furthermore the agreement is to within about six percent. This gives one a certain amount of confidence in the valence-force approximation.

No frequencies have been observed in the infrared, however, in the neighborhoods of the values calculated for ν_2, excepting those assigned to ν_1.

Table I. *Bond angle α_0,[6] observed infrared frequencies[7] and calculated frequencies in cm^{-1}, and calculated force constants in dynes/cm for NH_3, PH_3 and AsH_3.*

α_0	NH_3 109°		PH_3 96°		AsH_3 94°	
	obs.	calc.	obs.	calc.	obs.	calc.
ν_3 (‖)	950	1110 1010*	990	1050	906	960
ν_4 (⊥)	1631	(1631)	1121	(1121)	1005	(1005)
ν_1 (‖)	3335	(3335)	2327	(2327)	2122	(2122)
ν_2 (⊥)		3450		2340		2125
	4417 5059		3428		3091	
$K\times10^{-5}$		6.35		3.09		2.60
$H\times10^{-5}$		0.59		0.34		0.28

* Corrected for anharmonic term.

[4] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).
[5] F. Lechner, Wien. Berichte **141**, 633 (1932).

[6] The angle for NH_3 is known from spectroscopic data. The angles for PH_3 and AsH_3 were chosen on the basis of theoretical considerations and evidence from crystal structure given by Pauling, J. Am. Chem. Soc. **53**, 1367 (1931). No appreciable change is produced in the force constants by a change of a few degrees in the angles.
[7] Source of frequencies: NH_3—Schaefer and Matossi, *Das Ultrarote Spektrum*, p. 250. PH_3—Fung and Barker, Phys. Rev. **45**, 238 (1934). AsH_3—Robertson and Fox, Proc. Roy. Soc. **A120**, 149 (1928).
[8] M. F. Manning, J. Chem. Phys. **3**, 136 (1935).

Discussion of ν_2

NH_3

With the value of ν_2 calculated on the assumption of valence forces it is possible to explain the 4417 cm^{-1} infrared band as the combination $\nu_2\,(3450)+\nu_3\,(950)=4400$ cm^{-1} and, indeed, it is difficult to account for the band with any other combination of frequencies. The structure of the band is very irregular and does not admit a simple analysis.[9] Because of this complexity it is probably not a parallel-type band. Such bands have, in general, a relatively simple structure and are free of the distortions resulting from rotation-vibration interaction. Hence we must account for what is probably either a perpendicular-type structure or an overlapping of several bands. There appear to be only four alternative explanations. (a) The assignment $\nu_1\,(3335)+\nu_3\,(950)=4285$ cm^{-1} suggested by Badger and Mecke[10] leads to a parallel-type band and would not alone explain the structure. Now it is possible that the second overtone of $\nu_4\,(1631)$, *viz.*, $3\nu_4=4893$ cm^{-1} (minus the anharmonic terms), is stronger than the first overtone and accordingly might badly distort the parallel-type structure of this combination band. This alternative is improbable, however, because of the wide separation of the two frequencies involved. (b) There is the possibility that the second overtone of ν_4 gives rise by itself to the 4417 cm^{-1} band although this is doubtful since the band is almost as intense as the fundamental at 3335 cm^{-1}. (c) The combination $\nu_2\,(3450)+\nu_3\,(950)=4400$ cm^{-1} involving the valence-force value of ν_2 does, on the other hand, account for the frequency and intensity of the band, and leads to a perpendicular-type structure, the complexity of which would be increased by the doublet character introduced by the 950 cm^{-1} component. (d) The possibility that the 4417 cm^{-1} frequency is itself ν_2 is considered below.

In the Raman spectrum of gaseous NH_3 Lewis and Houston[11] have observed a line at a shift of 3219 cm^{-1} which they suggest may be ν_2. The difference between this frequency and the valence-force value calculated for ν_2 might conceivably be ascribed to the presence of cross terms of moderate size in the potential function. There are two bits of evidence, however, which conflict with the allotment of this line to ν_2. Firstly, Bhagavantam[12] finds that the corresponding line with 3208 cm^{-1} shift in the Raman spectrum of the liquid is very well polarized, a result which is incompatible with the assignment of this line to a degenerate vibration. Secondly, the combination $\nu_2\,(3219)+\nu_3\,(950)=4169$ cm^{-1} gives too low a frequency for the 4417 cm^{-1} band which is difficult to account for by another assignment.

Further support of the valence-force assignment for ν_2 is given by the frequencies of the CH_3 group in the methyl halides. The CH_3X molecule has two more frequencies than the NH_3-type molecule as a result of the additional atom X. If we allow the bond between C and X to vanish, however, these two frequencies will go to zero and, simultaneously, the vibrations of CH_3X will pass over into the vibrations of a free CH_3 molecule. In the spectra[13] of the methyl halides the four frequencies characteristic of the CH_3 group are readily identified. The strength of the C–X bond in each halide can be estimated from the observed frequency of vibration of the CH_3 group against X by using the diatomic model $(CH_3)-X$. For X equal to F, Cl, Br and I, the force constant for stretching of the C–X bond assumes the values 5.3×10^5, 3.3×10^5, 2.8×10^5 and 2.2×10^5 dynes/cm, respectively. Plotting these values against the observed frequencies of the CH_3X molecules and extrapolating to zero force-constant, we obtain the following approximate frequencies of vibration of a free CH_3 molecule: $\nu_3=900$ cm^{-1}, $\nu_4=1420$ cm^{-1}, $\nu_1=2985$ cm^{-1} and $\nu_2=3120$ cm^{-1}. These values are similar to the frequencies calculated for NH_3 upon the assumption of valence forces. The extrapolation does not, of course, take into account the consequences of the tunnel effect.

The most obvious difficulty with the valence-force value of 3450 cm^{-1} for ν_2 is that such a frequency does not appear in the infrared whereas

[9] E. F. Barker, private communication.

[10] R. M. Badger and R. Mecke, Zeits. f. physik. Chemie **B5**, 333 (1929).

[11] C. M. Lewis and W. V. Houston, Phys. Rev. **44**, 903 (1933).

[12] S. Bhagavantam, Ind. J. Phys. **5**, 49 (1930). For a discussion of the significance of the polarization of Raman lines see G. Placzek, Leipziger Vorträge, p. 71 (1931).

[13] The frequencies of the methyl halides are given by A. Adel and E. F. Barker, J. Chem. Phys. **2**, 627 (1934).

ν_2 is a theoretically active frequency. Very little is known, however, regarding the change of electric moment during vibration in such molecules as NH_3 and it cannot be said how serious a difficulty this is. The failure to appear in the Raman spectrum of the gas may be due merely to insufficient intensity; ν_4 (1631) is likewise not observed. It is commonly true that theoretically active, degenerate frequencies appear less intense in Raman spectra than frequencies of completely symmetric vibrations and in the case of compounds containing hydrogen are frequently not observed.

Another possible difficulty has been pointed out to the author by Professor Dennison. From the complete expressions derived by Salant and Rosenthal[14] for the symmetrical tetratomic molecule $Y^{(M)}X_3^{(m)}$ we obtain for two such molecules (denoted by single and double primes) the relation $(m\nu_2\nu_4)'^2/(m\nu_2\nu_4)''^2=(b/\mu)'/(b/\mu)''$, where $b=6\mu(c^2/a^2)+1$ and $\mu=M/(3m+M)$. Here c and a are the altitude of the pyramid and the side of the base, respectively. This relation must be satisfied rigorously as long as the potential functions of the two molecules remain purely quadratic. Assuming that the 4417 cm^{-1} band of NH_3 and the 3287 cm^{-1} band of ND_3[15] arise from the combination $\nu_2+\nu_3$, we obtain 3470 cm^{-1} and 2520 cm^{-1} as the values of ν_2 for NH_3 and ND_3, respectively. These frequencies, when substituted in the above relation together with the observed values of ν_4, lead to a ratio of 0.94 instead of 0.87 which is the value of the ratio of the (b/μ) term for NH_3 to that for ND_3. This difficulty is serious only if the centers ascribed to the observed bands for $\nu_2+\nu_3$ and ν_4 are correct and if our method of obtaining values for ν_2 is valid. It does not require a large change in the values used to yield a ratio 0.87. Thus the values $\nu_2=2565$ cm^{-1} and $\nu_4=1180$ cm^{-1} calculated below for ND_3 assuming valence forces give the correct ratio (since they are obtained from the NH_3 frequencies by using the formulas from which the above comparison relation is derived).

The 4417 cm^{-1} and 3287 cm^{-1} frequencies, on the other hand, give (as was pointed out by Professor Dennison) a ratio of 0.89, in closer agreement. A check of this sort does not, of course, imply that the frequencies used are the correct ones since only the ratios of the frequencies are tested. Nevertheless, this bit of evidence, together with the difficulty of explaining the 4417 cm^{-1} band as a combination other than $\nu_2\,(3470)+\nu_3\,(950)=4420$ cm^{-1}, indicates that if the assumption of valence forces does not give the correct value of ν_2, this frequency of 4417 cm^{-1} is probably the fourth fundamental. If such is the case then there is a very large departure from valence forces in passing from CH_4 or H_2O to NH_3.

PH_3 and AsH_3

No evidence is available regarding the valence-force interpretation of ν_2 in PH_3 and AsH_3. It seems probable from structural considerations, however, that the values of ν_2 in Table I, calculated using valence forces, will be equally good for these molecules and for NH_3.

Calculation of the Isotope Effect

If the valence-force frequency, $\nu_2=3450$ cm^{-1}, for NH_3 is approximately correct the assumption of valence forces should be sufficient to calculate the fundamental frequencies of the isotopic molecules NH_2D, ND_2H and ND_3. In making this calculation we have used the complete formulas derived by J. E. Rosenthal[14] for the vibrational frequencies of the symmetric tetratomic molecule YX_2X^*. Values of the force-constants, $K=6.42\times10^5$ and $H=0.59\times10^5$, were chosen so as to give the calculated frequencies $\nu_2=3470$ cm^{-1} and $\nu_4=1631$ cm^{-1} for NH_3. This value of ν_2 satisfies the relation ν_2+950 $cm^{-1}=4420$ cm^{-1}. Table II gives the results of the calculations. The letter A after a frequency of NH_2D or ND_2H indicates that it corresponds to a vibration which is antisymmetric with respect to reflection through a plane passing through the figure axis and the hydrogen isotope which differs from the other two. The other frequencies of NH_2D and ND_2H are symmetric with respect

[14] J. E. Rosenthal, Phys. Rev. **45**, 426 (1934); **47**, 235 (1935). These formulas are given in terms of the force constants of the general potential function. In making the calculation, the general constants were evaluated in terms of K and H by means of the expressions for the former given by E. O. Salant and J. E. Rosenthal, Phys. Rev. **42**, 812 (1932) on p. 819. To obtain agreement with the valence-force formulas[5] for YX_3 it was found necessary to change the negative sign before K_6 in the expression for D to a positive sign.

[15] Observed ND_3 frequencies taken from Silverman and Sanderson, Phys. Rev. **44**, 1032 (1933).

TABLE II. *Observed*[15] *and calculated fundamental frequencies in cm*$^{-1}$ *of* NH_3 *and isotopic molecules.*

NH_3	obs.	950	1631	3335	?	
	calc.	1010* / 1110	(1631)	3355	(3470)	
NH_2D	obs.	1025	1385A 1600	3400	2510	3470A
ND_2H	calc.	925	1230 1460A	2455	2565A	3435
ND_3	obs.	770	1158	2421	?	
	calc.	840	1180	2405	2565	

* Corrected for anharmonic term. All other calculated values in the first column are frequencies for vibrations of infinitesimal amplitude.

to this plane. The computed values of ν_3 will lie above the observed frequencies, as is found to be the case for NH_3, and will more closely resemble the frequencies of vibrations with infinitesimal amplitude.

The agreement between the frequencies calculated for ND_3 and the three observed frequencies is satisfactory. As we have noted above the band reported at 3287 cm^{-1} may be used to determine ν_2 and gives the value $\nu_2 = 2520$ cm^{-1}, in rough agreement with the calculated value.

OVERTONE-COMBINATION BANDS

The proximity of ν_1 and ν_2 in all three molecules would explain the fair success of efforts to interpret the spectra using only the three fundamentals which appear. An attempt to obtain further evidence regarding the valence-force value of ν_2 from overtone-combination bands is rather inconclusive as long as the structures of these bands or the actual appearance of the bands to be expected from certain combinations of fundamentals are not better known. Thus, for example, we have two possible explanations of the 5059 cm^{-1} band of NH_3. The assignment given by Badger and Mecke[10] is $\nu_1\,(3335) + \nu_4\,(1631) = 4966$ cm^{-1}. The alternative assignment is $\nu_2\,(3470) + \nu_4\,(1631) = 5101$ cm^{-1}. The former combination leads to a perpendicular-type band, the latter to a band with both perpendicular and parallel components. The structure of the band has been analyzed as perpendicular by Stinchcomb and Barker[16] but it is possible that the presence of a parallel component would be masked by the more complex perpendicular component.

The writer is indebted to Dr. E. Bright Wilson, Jr., and Professor D. M. Dennison for their helpful criticisms and suggestions in connection with this work.

[16] Stinchcomb and Barker, Phys. Rev. **33**, 305 (1929).

The Magnetic Susceptibility of Lithium Hydride

The Diamagnetism of Ionic Crystals

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The magnetic susceptibility of crystalline lithium hydride was measured at room temperature (300°A) and at 78°A and was found to be -4.60×10^{-6} per mole with practically no temperature coefficient. One theoretical prediction deviates from the experimental value by 90 percent and another by 130 percent. This discrepancy is interpreted as due mainly to a paramagnetism independent of the temperature which is present in all crystals and which has not been included in the calculations.

THE diamagnetic susceptibility of a mole of atoms or atomic ions may be expressed by

$$\chi = -(Ne^2/6mc^2)\Sigma_i\overline{r_i^2},$$

where χ is the susceptibility per mole, N is Avogadro's number, $\overline{r_i^2}$ is the mean square distance of the i'th electron from the nucleus, the summation extending over all electrons and e, m, c have their usual meanings. Several theoretical methods have been devised for evaluating $\overline{r_i^2}$; one is based on Hartree's method of self-consistent fields,[1] another is due to Van Vleck and Pauling[2] independently, and more recently, Brindley[2] has employed the approximate eigenfunctions of Slater. Angus[2] has also computed $\overline{r_i^2}$ with these eigenfunctions but in greater detail. The diamagnetic susceptibilities derived with these various methods are compared by Angus with the susceptibilities of the alkali halides in solution as measured by Ikenmeyer.[2] The susceptibilities of Pauling are from 10 percent to 60 percent and of Stoner from 50 percent to 80 percent higher than the experimental values. Most of the values of Brindley are also high while those of Angus fluctuate above and below the experimental values by a few percent.

All the theoretical methods deal with electronic systems subject to central forces such as isolated ions in field-free space and since the only data available refer to ions in crystals or in solutions, there is ever present the question of the validity of such comparisons. The chief reassurance has come from the (supposed) additivity of the ionic susceptibilities, suggesting magnetic independence between them, and further there seems as yet little reason to suspect considerable changes in the mean square radius when a gaseous ion takes its place in a crystal lattice.

In the hope of clarifying some of the uncertainties we measured the magnetic susceptibility of lithium hydride principally because it is the simplest of all ionic lattices.[3] And when its eigenfunction is determined a direct comparison with experiment will be available. It remains to be seen whether the eigenfunction of the crystal will be separable into the eigenfunctions of the ions in the lattice with sufficient accuracy. This separability is implicit in all previous investigations, a matter we shall discuss later. In terms of separate ions, it may be observed that the hydride ion is probably more sensitive than any other to changes in electrical environment. Hence a measurable difference in the susceptibility would probably accompany a change from the gaseous state to the crystalline and the ion might serve to indicate whether all ions undergo such changes.

MATERIALS

We have had the good fortune to obtain crystals of pure lithium hydride. They were furnished by the Maywood Chemical Works, Maywood, N. J., through the courtesy of Dr. H. Osborg. In the light of chemical and magnetic analyses, any ordinary paramagnetic impurity was present in less than 0.002 percent, probably much less, and diamagnetic impurities such as lithium hydroxide, sodium hydride made up less

[1] Stoner, cited by W. R. Angus, Proc. Roy. Soc. **A136**, 569 (1932).

[2] Cited by W. R. Angus, see reference 1.

[3] Hylleraas (Zeits. f. Physik **63**, 771 (1930)) has confirmed from the heat of sublimation that the lattice is ionic. The crystals are similar to sodium chloride, colorless, hard, melt at a rather high temperature (680°C), all in keeping with an ionic lattice. It was found to be cubic, NaCl type, (Bijvoet and Karssen, Proc. Amst. Acad. **31**, 496 (1922)).

than 0.5 percent of the material and could be ignored in magnetic considerations. Chemical analyses for the ferromagnetic impurities, iron and nickel, were made as these more than others were likely to contaminate the material on account of the method of manufacture. The presence of total iron, both free and combined, was found to be less than 7 moles iron in 10 million moles lithium hydride and probably less than 1 in 10 million. No trace of nickel was observed although 1 mole nickel in 5 million lithium hydride would have been detected. It is well known that ferromagnetic metals commonly lose their ferromagnetism when alloyed so that the best sign of ferromagnetic contamination is the magnetic behavior of the substance, the necessary criterion being a dependence of the susceptibility on the field strength. We are unable to observe such a dependence in our materials.

After the lithium hydride had been measured magnetically, it was taken out of the tube for chemical analysis. Different samples gave 99.4 percent, 97.5 percent, 99.5 percent an average of 98.8 percent lithium hydride. The impurities are probably lithium hydroxide and other alkali hydrides. The hydroxide is formed from the hydride and moisture. For this reason the utmost precautions were taken never to expose the hydride to moisture. All the necessary manipulations (such as grinding the crystals to a powder, tamping it into a glass tube for the magnetic measurements) were carried out in a "dry-box" through which dried gases were flowing. In selecting the crystals, any having a blue coloration were avoided. This color is a very sensitive indication of uncombined lithium metal. It is probable that even if some of the faintly blue crystals had been taken no difference would have entered into the magnetic results within our limits of error.

About six months after the first magnetic measurements were taken, we received some lithium hydride from the Maywood Chemical Works which had been made in a more recent lot. Dr. Osborg was good enough to have crystals selected for us which had little likelihood of having touched the metallic walls of the apparatus in which it was made. From these we further selected colorless crystals for the magnetic measurements.

Magnetic Measurements

The well-known method of Gouy was employed for the magnetic measurements and at low temperatures the method described by Freed.[4] The magnet was of the Weiss type kindly loaned us by Professor W. D. Harkins. It was built with the aid of a grant given to Professor Harkins by the Joseph Henry fund of the National Academy of Sciences. The first two sets of runs listed below were carried out with magnetic fields up to 23,000 gauss and in the remaining runs with fields up to 18,000 gauss.

The magnetic susceptibility was also determined at 78°A to enhance the effect of any paramagnetic impurity since paramagnetic susceptibility usually varies almost inversely as the absolute temperature. That is, the paramagnetic impurity would have its room temperature susceptibility almost quadrupled at 78°A.

As has been noted, we were unable to detect any variation in the susceptibility with field strength such as one would expect from the presence of any ferromagnetic impurity.

On May 21, 1934, the magnetic susceptibility per mole of lithium hydride was determined at room temperature (300°A) as -4.42×10^{-6}.

On May 22, 1934, another sample of the same crystals was taken and independent magnetic measurements at room temperature (300°A) gave -4.68×10^{-6} per mole. The deviations from the average of these two sets of runs is 3 percent, a little high, perhaps because of the irregularities in the packing of the powder in the tubes.

On December 10, 1934, lithium hydride which had been prepared afresh by the Maywood Chemical Works was measured under conditions which were very different from those which had prevailed in the other measurements. The glass tube containing the powder was changed, the pole gap of the magnet and hence range of magnetic fields were different. The susceptibility per mole was found in a series of runs as -4.65×10^{-6} in satisfactory agreement with the values obtained six months previously. These crystals had been measured in a Dewar vessel at room temperature. The temperature was then lowered to 78°A (the temperature of liquid nitrogen) and the susceptibility at this temperature was -4.60

[4] S. Freed, J. Am. Chem. Soc. **52**, 2702 (1930).

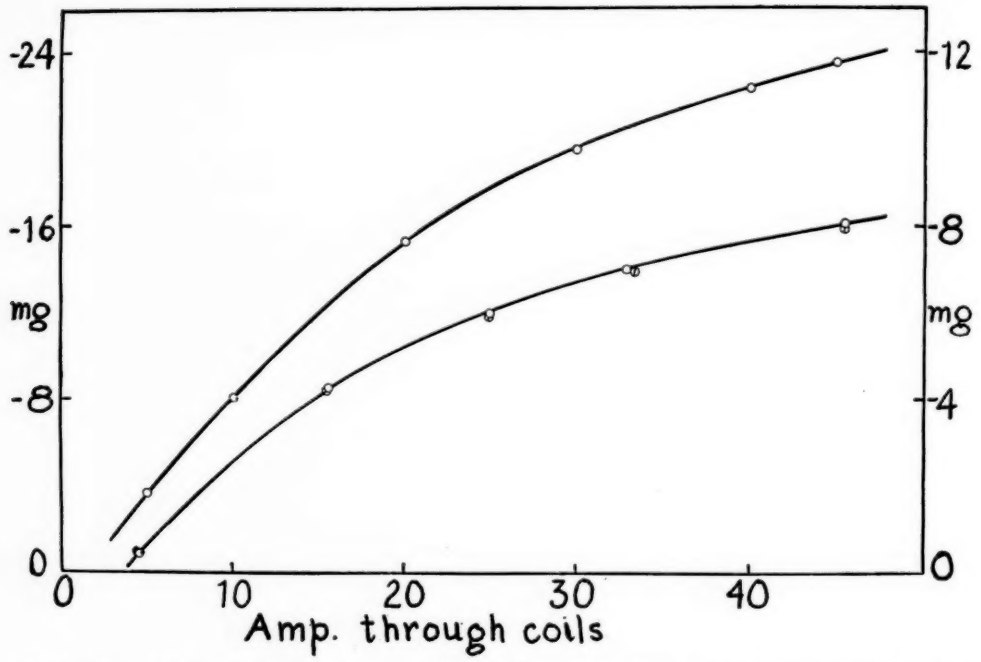

FIG. 1. Change in apparent weight in magnetic field. Water for calibration: upper curve, weight at left. Lithium hydride: lower curve, weight at right. Clear circles at room temperature 300°A. Halved circles at 78°A.

$\times 10^{-6}$, an increase of 1.1 percent. This difference is real as the experimental method is especially suitable for measuring differences resulting from changes in temperature. At room temperature, the percentage of the susceptibility which may be ascribed to a paramagnetic impurity is about $(78/222)\times 1.1 = 0.35$ percent. The deviations between measurements within a set of runs occurred in the third decimal place.

The figure gives the curves obtained from the measurements both of water, which served for calibration, and of lithium hydride at 300°A and at 78°A.

We conclude, then, that the molal susceptibility of lithium hydride in the crystalline state is -4.60×10^{-6} within about 2 percent.

DISCUSSION OF RESULTS

The molal susceptibility of lithium hydride predicted by Pauling is -8.65×10^{-6} and by both Brindley and Angus -10.54×10^{-6} and the experimental value is -4.60×10^{-6}, truly another order of magnitude. We are faced with several possibilities of which the more important are: (1) The mean square radii of the electrons in the ions (hydride ion, especially) have undergone a shrinkage of 50 percent or more; (2) a factor which does not operate in isolated ions introduces in crystals a paramagnetism which is practically independent of the temperature. On this basis the measured diamagnetic susceptibility cannot be related exclusively to the term of the mean square radii. This factor, we are inclined to believe, accounts for most of the discrepancy.[5]

[5] That there may also be a possible shrinkage in the $\overline{r_i^2}$ of the electrons is suggested by the fact that the radius of the hydride ion as defined for x-ray data is less in lithium hydride than in other alkali hydrides. Zintl and Harder (Zeits. f. physik. Chemie **B14**, 265 (1931)) give the following lattice distances for the alkali hydrides. Upon subtracting the radii of the positive ions as given by Zachariasen (Zeits. f. Krist. **80**, 137 (1931)) from one-half the lattice distance, the radii of the hydride ions are obtained. These are listed in the last column.

	Lattice distance	r_{M^+}	r_{H^-}
LiH	4.084	0.68	1.36
NaH	4.880	0.98	1.46
KH	5.700	1.33	1.52
RbH	6.037	1.48	1.54
CsH	6.376	1.67	1.52

It need not follow that there is any difference in the $\overline{r_i^2}$ of the electrons in the various hydride ions. Even if the effect on the $\overline{r_i^2}$ were as large as is here suggested, it would be small compared with the discrepancy between the computed and experimental susceptibilities and we are inclined to the view that the ignored possibility (2) is a dominant factor.

Van Vleck[6] has shown that in atomic systems having spherical symmetry, the instantaneous angular momentum of the $^1S_0$ state is zero as well as its average angular momentum. In polyatomic systems, among which we may include crystals, the instantaneous angular momentum is not zero, even when the stationary state is $^1\Sigma_0$ that is, even when the average angular momentum is zero. The perturbation theory foresees a paramagnetic contribution from the square of these instantaneous fluctuations in angular momentum which of necessity is positive. If the frequency differences between the various states is high as compared with kT this paramagnetism would be independent of the temperature. The magnitude of this "fluctuation" paramagnetism which we shall call the "Van Vleck paramagnetism" is in many instances great enough to account for the discrepancy between the experimental susceptibility and the various computed values. As examples we may cite the magnetic measurements[7] on $KMnO_4$, $K_2Cr_2O_7$, K_2MoO_4 and UO_2SO_4 which were selected to show this effect in MnO_4^-, $Cr_2O_7^=$, $MoO_4^=$ and UO_2^{++}. In these instances the paramagnetism was more than great enough to overbalance the total diamagnetism of the crystal and yet it was small compared with the usual paramagnetism which varies with the temperature.

There is no doubt that the alkali halides may undergo quantum transitions[8] to states associated with angular momentum. The same is doubtless true in lithium hydride[9] also. If we symbolize the NaCl lattice as

$$\begin{array}{l} Na^+Cl^-Na^+ \\ Cl^-Na^+Cl^- \\ Na^+Cl^-Na^+ \end{array}$$

upon absorbing ultraviolet light, the crystal is activated into a state thus,

$$\begin{array}{l} Na^+Cl^-Na^+ \\ Cl^-Na^0Cl^0 \\ Na^+Cl^-Na^+ \end{array}$$

to which the blue color has been ascribed.[8] Other transitions are possible also.

[6] J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford University Press, 1932.
[7] S. Freed and C. Kasper, J. Am. Chem. Soc. **52**, 4671 (1930).
[8] R. Hilsch and R. W. Pohl, Zeits. f. Physik **68**, 721 (1931).
[9] F. Bach and R. F. Bonhoeffer, Naturwiss. **20**, 940 (1932).

The final state we have been discussing is paramagnetic but it is not the number in the final state we are concerned with. It is rather the fluctuation from the basic state to the activated state which accounts for the paramagnetism independent of the temperature. The conclusion is then that some of the diamagnetism originating in the mean square radii is masked by the Van Vleck paramagnetism in all ionic crystals as well as in others; and that it is erroneous to employ experimental diamagnetic susceptibilities alone to furnish average radii of ions or to serve as criteria for the accuracy of such approximate eigenfunctions as have been proposed. In some instances, it is true such errors may not be great, a matter which requires separate investigation. Theories which furnish correct mean square radii would yield greater diamagnetic susceptibilities than are to be found experimentally and hence the values of Pauling or of Stoner should not be rejected because of "poor agreement" with the experimental susceptibilities.

From this point of view, we would expect the additivity of ionic susceptibilities not to hold except as a rough approximation especially among dissimilar compounds. One would expect some difference between the diamagnetism of crystals and of their solutions and possibly also, but to a much lesser degree, some departure from linearity in the susceptibility as a function of the concentration in regions of high concentration.

Very opportunely, Hoare[10] has remeasured with considerable care the diamagnetic susceptibilities of salts with rare gas ions and we shall quote some of his conclusions:

> It will be seen then that no conclusive evidence as to the validity of the additivity principle can be derived from this table, especially from Ikenmeyer's results; the results of the present investigation indicate, however, that it may be true to a first approximation.
>
> Hocart measured the susceptibilities of the chlorides in the crystalline form and in aqueous solution, finding the results in the former state to be less than the latter. It would appear, therefore, from the results for the bromides and iodides, that the result found by Hocart for two salts might very well be in agreement with a general principle. This conclusion is strengthened by Kido's results.

[10] F. E. Hoare, Proc. Roy. Soc. **A147**, 88 (1934).

A Plant for the Production of Heavy Water

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(Received February 14, 1935)

A description is given of a plant for the production of deuterium oxide by the electrolytic method which operates with a higher efficiency than has been previously reported for this method. The fractionation factor, uncorrected for evaporation, averages 8.6. Steel cells, which also serve as the cathodes, are used and the entire construction is explosion-proof.

SEVERAL types of laboratory equipment for the production of deuterium oxide by the electrolytic method have been described.[1] To these published accounts we wish to add the following brief description of a plant recently constructed in this laboratory which may be of interest because we are able to report a higher efficiency than is usually realized in the electrolytic separation of hydrogen and deuterium.

This plant consists of 37 water-cooled steel cells of 3 l capacity each, operated in series at 100 amperes, and arranged in three stages, and one smaller cell of 800 cc capacity which constitutes the fourth and final stage. The gases generated in each stage are collected by iron header pipes and are conducted successively through spray traps and explosion traps into air-cooled burners in which recombination takes place. The entire construction is sufficiently rugged to withstand explosions without damage.

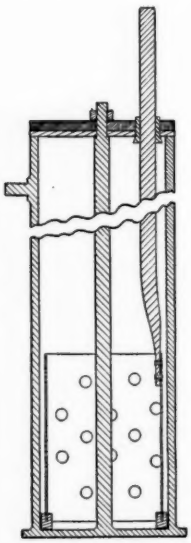

FIG. 1. Cross-sectional diagram of cell.

It was intended that this plant should operate on water already enriched to the extent of 0.5 percent deuterium oxide and with this as the starting material four stages suffice to increase the concentration to 99.9 percent, the daily production then being approximately 90 grams. However, the inadequate supply of 0.5 percent water frequently necessitates operation on water of considerably lower concentration and the average production falls far short of the figure mentioned.

DESIGN OF THE CELLS*

The cells are constructed of Shelby seamless steel tubing, 4″ in diameter and 18″ in length. A bottom plate and a central tie-rod which secures the lid are attached by arc welding. The lid carries a gas outlet tube and a tube through which the cell is filled and drained (these tubes are not shown in the accompanying sketch). The cell itself, insulated from the cooling water by paint, serves as the cathode. The anode consists of a perforated cylinder of sheet nickel, $3\frac{1}{2}$″ in diameter and 5″ high, attached by nickel rivets to the flattened end of a $\frac{1}{2}$″ nickel rod which passes through an inverted rubber stopper in the lid of the cell. The nickel cylinder is insulated from the cell wall by small pieces of hard rubber. The small cell which constitutes the fourth stage is constructed on the same design but the material is $2\frac{1}{2}$″ iron pipe.

The current density at the cathode varies with the level of the liquid in the cell. At the anode

[1] G. N. Lewis and R. T. MacDonald, J. Chem. Phys. **1**, 341 (1933); H. S. Taylor and H. Eyring, Proc. Am. Phil. Soc. **72**, 255 (1933); H. S. Taylor, H. Eyring and A. A. Frost, J. Chem. Phys. **1**, 823 (1933); W. D. Harkins and C. Doede, J. Am. Chem. Soc. **55**, 4330 (1933); L. C. Anderson, J. O. Halford and J. R. Bates, J. Chem. Phys. **2**, 342 (1934.)

* The design of the cells was worked out by Dr. D. Rittenberg and Dr. S. H. Manian.

the current density is approximately 0.28 ampere/cm² when this electrode is completely immersed, and it increases to about twice this value at the end of a run when only half immersed.

Before use the cells were cleaned by electrolysis of a hot solution containing 30 grams each of borax and trisodium phosphate per liter. This treatment together with the care taken to ensure the purity of the solutions used subsequently in the cells appears to be effective in preventing foaming.

Construction of the Burners

The gases generated in the cells of the first stage pass into iron header pipes which are connected to the cells by short sections of heavy wall rubber tubing. There are three separate header assemblies for this stage, each collecting the gas from ten cells. From these the gases pass through spray traps packed with steel wool, then through explosion traps filled with 60-mesh sand, and finally through jets at which recombination takes place. The first stage burner consists of a fan-cooled 3″ iron pipe mounted at a slight incline. A cap fitting over the upper end carries the three converging jets which project into the pipe. At the lower end a nipple conducts the steam into vertical water-cooled condensers. The jets consist of $\frac{1}{4}$″ iron plugs through which holes of 0.090″ diameter have been drilled and which are threaded into the $\frac{3}{8}$″ iron pipes projecting through the burner cap. The explosion traps are mounted rigidly on the burner cap and are connected to the spray traps by rubber tubing thus permitting the cap to be withdrawn for lighting. The entire assembly, with the exceptions mentioned, is constructed of standard plumbing fittings.

The second stage burner is similar in size and construction and the principle of multiple converging jets is retained by having two jets, each fed by three cells, with separate headers and traps. The orifice in these jets is 0.050″ in diameter.

The third and fourth stage burners are smaller in size, each having a single gas jet. The orifices are 0.028″ and 0.015″, respectively, the sizes being somewhat critical with the smaller gas flow in these burners.

Electrical Equipment

The cells are connected in series and are operated from a 110-volt line, the current being controlled by a rheostat of 0.4 ohm resistance. An underload circuit breaker prevents the resumption of the electrolysis should an interruption in the current sufficient to extinguish the burners occur. The fourth stage cell takes approximately one-half of the current used in the other cells (100 amperes), the remaining half being passed through a shunt. This stage and the third stage are provided with short-circuiting switches allowing these stages to be switched in or out as desired. The fourth stage is operated only when attended, but the remainder of the plant is operated overnight regularly without attention.

Operation of the Plant

The thirty cells of the first stage are charged with 3 l each of a 3 percent sodium hydroxide solution made up of the water to be concentrated. The sodium hydroxide is a C.P. Electrolytic grade, and the water is distilled once or twice before use. When it appears desirable a distillation from alkaline permanganate is carried out. The charges are measured out and placed in the cells with the aid of a portable apparatus built for this purpose.

When the electrolysis has proceeded for approximately 72 hours, this charge, totalling 90 liters, will have been reduced to about one-sixth of its original volume. It is then removed, a part of it distilled and then transferred to the second stage. Similarly the residue from the second stage is transferred to the third, and so on. A charge of 90 l of water containing 0.5 percent deuterium oxide will yield 15 l of approximately 2.5 percent. In the second stage the concentration will have increased to about 12 percent, in the third to about 60 percent and in the fourth to better than 99 percent.

The disposal of the recombined water depends upon its concentration. Normally the water used in the first stage contains from 0.3 percent to 0.5 percent deuterium oxide and except for the first fraction the recombined water contains an appreciable amount of deuterium. It is our practice to discard recombined water containing less than 0.05 percent deuterium, and to re-

work the remainder. Recombined water from the later stages is returned to the previous stage.

Fractionation Factors

Samples of recombined water are collected from each stage at the end of each run. These, as well as samples from the residues, are analyzed interferometrically[2] for their deuterium content providing data from which the fractionation factors may be calculated. Data for a number of typical runs are given in Table I, together with

Table I.

Run	Residue % D_2O	Recombined % D_2O	Fractionation factor
	First stage		
1	2.27	0.30	7.7
2	2.66	0.32	8.5
3	1.19	0.15	8.0
4	2.53	0.25	10.3
9	2.67	0.25	10.9
11	1.83	0.22	8.5
12	1.91	0.26	7.5
	Second stage		
1	2.23	0.25	8.5
2	2.91	0.31	9.1
3	13.3	2.10	7.1
4	9.41	1.29	7.8
5	4.49	0.56	8.1
7	11.6	1.52	8.4
9	7.53	0.85	9.3
12	13.5	1.79	8.5
13	6.59	0.82	8.4
	Third stage		
1	50.3	10.3	8.8
5	35.1	5.72	8.9
6	62.6	15.6	9.0
9	67.8	16.8	10.4

the fractionation factors. These are the instantaneous factors, and in a number of cases they have been checked by calculations of the overall factors, that is, the factor which must be substituted in the integrated Rayleigh distillation formula to satisfy this relation between the initial and final volumes and concentrations. In most cases, however, we have not sufficient data to calculate the overall factor since the runs are rarely straight runs. It happens almost always that the electrolysis is stopped one or more times during the course of a run to add recombined or other water of appropriate concentration. Thus a first stage run might be started with a charge of 0.15 percent water, to which would later be added 0.30 percent water, and perhaps later 0.50 percent water.

The average value of the fractionation factors listed in Table I is 8.6. This is appreciably higher than any previously reported.[1,3] These values have not been corrected for evaporation. Since the temperature in the cells averages about 25°C such a correction would increase the average fractionation factor to approximately 12. Presumably this high factor could be realized by cooling the gases leaving the cells so as to collect water carried over as water vapor, but we have not yet attempted to do this.

Purification of Heavy Water

The residue from the fourth stage, after having been neutralized and distilled, is not sufficiently pure for many experimental purposes. It contains traces of organic impurities not readily removable by distillation or by refluxing with oxidizing agents, and to effect the purification we make use of an additional stage of electrolysis. In this apparatus the deuterium and oxygen generated by electrolysis in a small iron cell are mixed with an excess of pure oxygen and burned at a silica jet inserted in a Pyrex condenser. The apparatus is flushed with oxygen before electrolysis is begun and with this precaution the oxides of nitrogen, customarily present in recombined water, are excluded.

This plant was constructed and is being operated under a grant-in-aid of heavy water research by the Rockefeller Foundation. In the design and construction of it we have enjoyed the cooperation of Professor H. C. Urey, Professor J. E. Zanetti, Dr. D. Rittenberg and other members of the staff of this laboratory.

[2] R. H. Crist, G. M. Murphy and H. C. Urey, J. Chem. Phys. **2**, 112 (1934).

[3] R. P. Bell and J. H. Wolfenden, Nature **133**, 25 (1934); B. Topley and H. Eyring, Nature **133**, 292 (1934), J. Am. Chem. Soc. **55**, 5058 (1933), J. Chem. Phys. **2**, 217 (1934); P. Harteck, Proc. Phys. Soc. **46**, 277 (1934).

The Thermal Conductivity of Polyatomic Gases

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(Received December 12, 1934)

Reasons are given for supposing that the thermal conductivity of polyatomic gases should not be independent of pressure. A calculation is made for carbon dioxide, and the results suggest that a portion of the specific heat at 0°C has a relaxation constant considerably less than 10^6 if the discrepancy between experimental and theoretical values of thermal conductivity is due to restrictions on the energy exchange between molecules. When such effects are present, determinations using parallel plates give a more reliable result than those using a vertical wire.

A KNOWLEDGE of the mechanism of heat transport in gases is important both in the kinetic theory, and in many chemical reactions involving activated molecules. The object of the present communication is to discuss the transport of vibrational heat in gases, and to point out that the thermal conductivity of polyatomic gases may vary with pressure. This is because of the fact that at higher pressures any departure from the Maxwell Boltzmann distribution of energies is more rapidly readjusted. A calculation is given for the heat transport between two parallel plates, and when certain simplifying assumptions are made, it is shown that the thermal conductivity K at any pressure is related to the maximum value K_{max} with full participation of the vibrational energy, by an equation of the form $K(1+F)=K_{max}$. The factor F depends on the pressure and dimensions of the apparatus, and has been evaluated in a typical case for CO_2. The bearing of this calculation on previously obtained experimental data for the thermal conductivity of polyatomic gases is discussed, and it is pointed out that empirical pressure corrections may be misleading. A correlation of the relaxation time for redistribution of vibrational energy in CO_2, as calculated from the dispersion of sound at high frequencies, with that calculated from thermal conductivity, is shown to be reasonable, though a quantitative check is hampered by lack of suitable experimental data.

Two methods are available for determining how far vibrational energy of the molecules of a gas takes part in heat transport. According to views developed by Eucken[1] if K is the thermal conductivity of a gas, C the specific heat at constant volume, and η the viscosity, the factor f in the equation $K=f\eta C$ may be calculated. The translational energy is assumed to be transported according to the Chapman-Enskog formula $K_{trans}=2.5\eta C_{trans}$, and if both rotational and vibrational transport are independent of translational,

$$K=(K_{trans}+K_{rot}+K_{vib})$$
$$=\eta(2.5C_{trans}+C_{rot}+C_{vib}).$$

If $\gamma=C_p/C$, $C=R/(\gamma-1)$,

and

$$f_{(Eucken)}=(2.5C_{trans}+C_{rot}+C_{vib})/(C_{trans}+C_{rot}+C_{vib})$$

i.e., $f_{(Eucken)}=1+1.5C_{trans}(\gamma-1)/R=\frac{1}{4}(9\gamma-5)$.

If vibration takes no part in heat transport but is operative in experiments determining C and γ,

$$f_{(no\ vib)}=(2.5C_{trans}+C_{rot})/(C_{trans}+C_{rot}+C_{vib})=(21/4)(\gamma-1)$$

for polyatomic and $(19/4)(\gamma-1)$ for linear molecules.

A test of this calculation requires a precise knowledge of thermal conductivity, viscosity and specific heats, all at the same temperature and pressure. Such a calculation is possible for CO_2.[2] For other gases included in Table I less

TABLE I.

Gas	CO_2	N_2O	CO	CH_4	C_2H_4	C_2H_2	C_2H_6	H_2S	NH_3
f (Eucken)	1.72	1.73	1.91	1.68	1.57	1.59	1.50	1.72	1.70
$K/\eta C$	1.64	1.71	1.92	1.69	1.43	1.42	1.54	(1.37)	(1.38)
f (no vib)	1.52	1.55	1.92	1.60	1.34	1.37	1.16	1.68	1.63

[1] Eucken, Physik. Zeits. **14**, 324 (1913).

[2] Kannuluik and Martin, Proc. Roy. Soc. **A142**, 362 (1933).

reliable data are available.[3] Except in the last two cases, where there may be serious error in the data, the value of f calculated from $K/\eta C$ lies between the two theoretical limits. For $(C_2H_5)_2O$ and gases with smaller γ the effect is still more marked but the data less reliable. Eucken has suggested that the value of f is due to the fact that vibrational and in some cases even rotational energy is not taking full part in heat transport, owing to incomplete temperature equilibrium. A second method is now available to test this, since experiments on the velocity of sound in such gases as CO_2 show that at ordinary temperatures and pressures dispersion sets in in the neighborhood of 10^5 cycles/sec. One explanation is that at still higher frequencies the vibrational energies are no longer able to follow the adiabatic temperature changes in a sound wave.

During the interval of 10^{-5} sec., the average distance diffused by a molecule may be calculated from the formula $\bar{x}^2=2Dt$. For CO_2 at 0°C and 20 cm of mercury, $D=0.4$ and $x=3\times10^{-3}$ cm, i.e., some 100 mean free paths. In such a case it is clear that in the parallel plate method for determining the thermal conductivity of a gas, we cannot assume complete equilibrium for the vibrational energy in various layers. In order to clear up certain difficulties in interpreting experiments on the dispersion of sound[4] and on thermal conductivity[5] it is important to correlate the two phenomena as far as possible.

Consider an experiment where the heat transport in a gas between two parallel plates is measured. If Q is the heat transport/unit area, and the plates are a distance z_0 apart, and are maintained at temperatures T_{P_1} and T_{P_2}, the experimentally determined thermal conductivity is obtained from the equation $Q=K\Delta T_P/z_0$ where $\Delta T_P=T_{P_1}-T_{P_2}$, and K is the mean value of the thermal conductivity over small ranges of temperature. This value of K may differ from that calculated from the kinetic theory of gases for one of two reasons:

(1) The average temperature T_V characterizing the distribution of vibrational energies in any layer will differ from the temperature T characterizing the distribution of rotational and translational energies by an amount $L=T-T_V$ (see below).

(2) Because of temperature jumps at the surface, the difference $\Delta T=T_1-T_2$ and still more so $\Delta T_V=T_{V_1}-T_{V_2}$ may be appreciably less than the measured difference $\Delta T_P=T_{P_1}-T_{P_2}$.

At sufficiently high pressures the problem is best considered as a case of diffusion in the steady state. If the molecules are distributed N_1, N_0/unit volume, in classes characterized by vibrational energies E_1, E_0 (in many cases it is sufficient to consider only two levels), then in the steady state the rate of increase of N_1/unit volume by diffusion is

$$D(\partial^2N_1/\partial z^2)=(\partial N_1/\partial t)_{\text{diff}} \qquad \text{(a)}$$

and must be balanced by the net rate of removal within the layer by collisions, i.e.,

$$(\partial N_1/\partial t)_{\text{diff}}+(\partial N_1/\partial t)_{\text{coll}}=0,$$

where $(\partial N_1/\partial t)_{\text{coll}}$ is a function of the composition of the layer. For the rotational and translational degrees of freedom, $(\partial N_r/\partial t)_{\text{coll}}$ is usually assumed to be negligible, because of the displacement from a Maxwell Boltzmann distribution being so small, the use of a temperature parameter T to characterize this distribution is thus allowable. With respect to these degrees of freedom we then have for each class 1, 2, etc.

$$D(d^2N_r/dz^2)=0 \text{ and } dN_r/dz=\text{const}=k_{N_r}. \qquad (a_1)$$

Since the net number of molecules crossing any layer in unit time is $D(dN_r/dz)$ the heat transfer

$$Q=\Sigma DE_r(dN_r/dz)=D\Sigma E_r(dN_r/dz)$$

if on the average D is independent of class (i.e., neglecting the Chapman correction). Integrating a_1 over the distance z_0 between the plates,

$$(N_r)_1-(N_r)_2=k_{N_r}z_0,$$

so that

$$Q=(D/z_0)\Sigma E_r[(N_r)_1-(N_r)_2].$$

If equilibrium is fully established at the plates,

$$\Sigma E_r[(N_r)_1-(N_r)_2]=NC_V(T_1-T_2)$$

and

$$Q=NDC_V(T_1-T_2)/z_0.$$

The standard formula is thus obtained.

We are, however, concerned with a degree of

[3] Landolt Bornstein Tabellen 5th ed.
[4] Richardson, Proc. Roy. Soc. **A146**, 56 (1933); Richards and Reid, J. Chem. Phys. **2**, 194 (1934).
[5] M. Trautz, Ann. d. Physik **18**, 833 (1933).

freedom for which $(\partial N_1/\partial t)_{\text{coll}}$ is not negligible, on account of the finite lag L. The vibrational temperature T_V will be defined by $N_1/N_0 = e^{-(E_1-E_0)/kT}$ and the calculation be made for a gas where the rate of relaxation is given by

$$\partial T_V/\partial t = \beta(T-T_V).^6 \qquad \text{(b)}$$

Furthermore, over the small intervals of temperature which have to be used in thermal conductivity experiments

$$\rho C_{\text{vib}} = (E_1-E_0)(dN_1/dT_V) \qquad \text{(c)}$$

will be appreciably constant, where C_{vib} is the vibrational specific heat/unit mass, and ρ is the density.

In the steady state, the heat transport Q through any layer is constant, i.e.,

$$-Q/NmD = C'(dT/dz) + C_{\text{vib}}(dT_V/dz) = b \qquad \text{(d)}$$

where b is independent of z, so that

$$C'T + C_{\text{vib}}T_V = bz + d \qquad \text{(e)}$$

where d is a constant. In (d) and (e), if we use the normal coefficient of diffusion, D, $C' = 2.5C_{\text{trans}} + C_{\text{rot}}$ in view of the Chapman correction. Combining (a) with (c), and using (b),

$$\begin{aligned} D(d^2N_1/dz^2) &= [\rho C_{\text{vib}}/(E_1-E_0)](\partial T_V/\partial t)_{\text{diff}} \\ &= [-\rho C_{\text{vib}}/(E_1-E_0)](\partial T_V/\partial t)_{\text{coll}} \\ &= -[\rho C_{\text{vib}}/(E_1-E_0)]\beta(T-T_V). \end{aligned} \qquad \text{(f)}$$

Substituting for T by means of (e), and noting

$$d^2N_1/dz^2 = [\rho C_{\text{vib}}/(E_1-E_0)](d^2T_V/dz^2),$$

$$D(d^2T_V/dz^2) = -(\beta/C')((bz+d)-(C_{\text{vib}}+C')T_V).$$

The solution to this equation is

$$T_V = Ae^{\alpha z} + Be^{-\alpha z} + (bz+d)/(C_{\text{vib}}+C'), \qquad (g_1)$$

where

$$\alpha^2 = \beta(C_{\text{vib}}+C')/C'D,$$

or since $L = T-T_V$, from (e) the solution simplifies to

$$L = Ae^{\alpha z} + Be^{-\alpha z}, \qquad (g_2)$$

where the arbitrary constants are different from those in (g_1). The third term in (g_1) is equivalent to a linear temperature gradient for T_V, and the first two take account of relaxation effects, as measured by the constant β in the equation for α^2.

In order to apply this solution to a concrete case, we have to evaluate the arbitrary constants by considering the boundary conditions. Since the system is symmetrical, when

$$z=0, \quad L = L_1 = A+B$$

and when

$$z=z_0, \quad L = -L_1 = Ae^{\alpha z_0} + Be^{-\alpha z_0},$$

whence

$$B = -Ae^{\alpha z_0}, \quad \text{and} \quad L_1 = A(1-e^{\alpha z_0}). \qquad \text{(h)}$$

The constant A can be evaluated by considering the change in energy of the molecules by collision with the plates. If the lag is appreciable, the vibrational temperature of the molecules approaching the plate will be appreciably different from that of the plate itself, even at ordinary pressures. According to the theory of the accommodation coefficient[7] if T_V be the (vibrational) temperature of the molecules approaching the plate, and T_0 that of the molecules leaving it,

$$T_D - T_V = a_{\text{vib}}(T_P - T_V),$$

where a_{vib} is the accommodation coefficient for vibrational energy. Little is known of the values of a_{vib}, but unless the material of the plates absorbs the molecules strongly, a_{vib} is probably very small because of the small duration of contact with the plate. By neglecting it altogether, the maximum value L_1 can have will be obtained and can be calculated. The rate of increase of N_1 in a layer of unit area and thickness dz next to the walls will be

$$\begin{aligned} &[\rho C_{\text{vib}}/(E_1-E_0)]D(dT_V/dz)_0 \\ &\quad + [\rho C_{\text{vib}}/(E_1-E_0)]\beta L_1 dz \\ &+ (N\bar{c}/4)[\rho C_{\text{vib}}/(E_1-E_0)]a_{\text{vib}}(T_P-T_V) = 0. \end{aligned}$$

In this equation the first term represents the net increase of N_1 by diffusion, which for this layer is equal to the net number of molecules crossing its boundary, $D(dN_1/dz)_0$. The second represents the change in N_1 by collisions in the gas, and the third by collisions with the plate. $N\bar{c}/4$ is the

[6] Rutgers, Ann. d. Physik **16**, 351 (1933).

[7] Knudsen, Ann. d. Physik **34**, 593 (1911).

number of molecules approaching the plate/unit time. If a_{vib} is negligible, $(dT_V/dz)_0=0$. Differentiating (g_1) and writing

$$z=0, \quad (dT_V/dz)_0=0,$$

$$(dT/dz)_0=\alpha(A-B)=\alpha A(1+e^{\alpha z_0})$$

and from (d), making the same substitution,

$$C'(dT/dz)_0=-Q/NmD.$$

Using these equations, and substituting for A from (h),

$$\alpha L_1(1+e^{\alpha z_0})/(1-e^{\alpha z_0})=-Q/NmDC'. \quad \text{(i)}$$

On inserting limits in (e),

$$C'\Delta T+C_{vib}\Delta T_V=Qz_0/NmD,$$

and since

$$\Delta T_V=T_{V_1}-T_{V_2}=T_1-L_1-T_2+L_2=\Delta T-2L_1,$$

$$\Delta T(C'+C_{vib})-2L_1C_{vib}=Qz_0/NmD. \quad \text{(j)}$$

Eliminating L_1 from (i) and (j),

$$\Delta T(C'+C_{vib})=z_0Q(1+F)/NmD, \quad \text{(k)}$$

where

$$F=(2C_{vib}/\alpha z_0C')(e^{\alpha z_0}-1)/(e^{\alpha z_0}+1).$$

Since equation (k) may be written,

$$Q=(C_{vib}+C')(\Delta T/z_0)\cdot NmD/(1+F),$$

and $$K_{max}=NmD(C_{vib}+C'),$$

we have $$K=K_{max}/(1+F).$$

The only other correction, for the difference $\Delta T_P-\Delta T$ is proportional to λ/z_0 where λ is the mean free path, and is usually negligible at the pressures used.

For a concrete case, inspection of the above correction term F shows:

(1) When $\alpha \ll 1$, indicating a large time of relaxation,

$$F=(2C_{vib}/\alpha z_0C')\times(\alpha z_0/2)=C_{vib}/C'.$$

In this case

$$K=K_{max}C'/(C'+C_{vib})=NmDC'$$

as would be expected when vibration takes no part in heat transport.

(2) When α is very large, $F=0$, as would be expected when vibration takes its full share in heat transport. It is important to know the region of pressures over which K is changing with pressure. Consider the case of CO_2 at 0°C in an apparatus for which $z_0=0.3$ cm

$$\beta=8.1\times10^5 \text{ at } 30° \text{ and } 760 \text{ mm},$$

$$C_{vib}=1.7, \quad C_{TR}=5.1=C_{rot}+C_{trans}.^6$$

By using the data of Richards and Reid[4] for the activation energy of vibrational transfer, $\beta=2.7\times10^5$ at 0° and 760 mm and at a pressure p mm Hg, $\beta=2.7p\times10^5/760$.

D at 0° and 760 mm $=0.1$ and at p mm Hg,

$$D=76/p.$$

Since $C_{TR}=5$ the molecule is taken as linear in calculating C'. From these data,

$$\alpha^2=(2.7\times10^5/76)p^2\times11.2/9.5=4.2p^2$$

and

$$F=(e^{0.61p}-1)/2p(e^{0.61p}+1)$$

when $p=0.1$ mm, 1 mm, 10 mm and 100 mm, the values of F are 0.152, 0.148, 0.05 and 0.005, respectively. The experimental value of F calculated from

$$1+F=f_{(Eucken)}/K/\eta C$$

is approximately 0.05 for CO_2.

Discussion

A comparison of these figures with the experimental value 0.05 for CO_2 which is obtained in the neighborhood of 200 mm, suggests that the value of β from acoustical experiments may have been overestimated. This is in part explained by assuming with Eucken and Mücke[8] that the vibration with $\theta=1830$ is not excited even at acoustical frequencies of 10^3 cycles. This would lead to a maximum of 0.02 to F at 0°C over the whole range of pressures considered above.

At present a more exact comparison is not possible, owing to the fact that the experimental methods commonly used for determining thermal conductivities are open to objection when used

[8] Eucken and Mücke, Zeits. f. physik. Chemie **B18**, 186 (1932).

for polyatomic gases. When concentric cylinders are used instead of parallel plates, Eq. (d) has to be modified to

$$-Q/2\pi rNmD = C'(dT/dr) + C_{\text{vib}}(dT_V/dr),$$

where Q is the heat transfer/unit length of axis. This leads to integrals in the solution which have to be evaluated for definite values of the variables. The solution is not given here, however, since most methods with concentric cylinders require a correction for the temperature jump, particularly at the surface with the smaller radius of curvature. According to Gregory and Archer[9] the most satisfactory form of the correction for simple gases is to write $\Delta T/(z_0+S)$ for the temperature gradient in place of $\Delta T/z_0$. S is taken as proportional to $1/p$. This correction is quite empirical and resembles the equation for F sufficiently to make a disentanglement of the two effects somewhat problematical; for evidence that this empirical correction alone is not adequate for CO_2 cf. M. Trautz.[5]

Independent evidence of the connection between thermal conductivities and the relaxation time for the various degrees of freedom can be obtained by considering the effect of small amounts of certain impurities. Thus the addition[4] of small amounts of H_2 and H_2O can increase β by several powers of 10; this should have the effect of increasing the thermal conductivity and decreasing the pressure coefficient.[10] Such an effect has actually been observed[11] though here again the use of the vertical wire method makes it uncertain whether it is to be ascribed to convection effects, to a change of the accommodation coefficient in the presence of hydrogen, or to the effect discussed in this communication.

[9] Gregory and Archer, Phil. Mag. **15**, 301 (1933).

[10] Ubbelohde, Proc. Roy. Soc. **A146**, 271 (1934).
[11] M. Trautz and S. Weber, Ann. d. Physik **54**, 498 (1917).

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On the Definition of the Gibbs Potential

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IN a short note *On the Definition of the Gibbs Potential*[1] in which I commented on recent criticism by some authors as regards the introduction by Willard Gibbs of the chemical potential into thermodynamics, I included the following remarks concerning an article by L. J. Gillespie and J. R. Coe, Jr.:[2] "Quite recently thermodynamic relations of open systems have been deduced by L. J. Gillespie and J. R. Coe. They avoid intentionally the Gibbs potential as a basis for their deductions, on account of the fact that 'Gibbs' treatment has been held obscure by some authors.' They say that Gibbs provides a physical interpretation (of the potential), but postpones it to a later part of his work." As Professor Gillespie has kindly called to my attention that these remarks might be interpreted as classing the two authors as critics of Gibbs, while the method adopted by them, avoiding the use of the potential, contained no such criticism, but was chosen for the sake of symmetry in the treatment, I am desirous to state that my remarks regarding the treatment of the two authors had no intention of such a classification.

On the contrary I am aware that the physical interpretation of the chemical potential, which follows from a rigid analysis of the mathematical definition by Gibbs suggests itself also as a consequence of an analogous interpretation of the energy and entropy functions of open systems given by Gillespie and Coe.

[1] J. N. Brönsted, Det Kgl. Danske Videnskabernes Selsk. Mathem.-Fys. Medd. **12**, No. 6, Copenhagen (1933).
[2] L. J. Gillespie and J. R. Coe, Jr., J. Chem. Phys. **1**, 103 (1933).

The Resolution of Bond Eigenfunctions in Terms of a Linearly Independent Set

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By means of simple operators derived from the antisymmetrical configuration eigenfunctions a method is devised for obtaining the coefficients in the expansion of a bond eigenfunction in terms of a linearly independent set. This method eliminates any necessity of drawing diagrams and removes the unique advantage of the uncrossed set. It is applied to the determination of the coefficients of eigenfunctions expanded in terms of the Rumer (uncrossed) set for as many as six bonds. For three and four bonds crossed sets are given for which the process of resolving eigenfunctions is simpler than for the Rumer set. A convenient method of expansion in terms of the Rumer set is extended to include eigenfunctions of as many as six bonds of any multiplicity.

I. INTRODUCTION AND GENERAL METHOD

IN order to take advantage of molecular symmetry in reducing the secular determinants of many atom problems it is necessary to be able to expand bond eigenfunctions in terms of a complete set. Until quite recently the calculation of the coefficients in such an expansion offered considerable difficulty. A solution of this problem, complete from the theoretical point of view, has been given by Rumer, Teller and Weyl[2] who developed a geometric method of determining such a complete set and also show how by the laborious method of successive uncrossing of bonds, any eigenfunction can be expanded in terms of an uncrossed set. Their methods have been applied to the less complicated symmetrical molecules. As the number of bonds considered is increased the process rapidly reaches Herculean dimensions. Preceding papers from this laboratory have given rules for getting the coefficients in the expansions of eigenfunctions containing as many as six bonds in terms of the Rumer set.[3] These methods, however, enable one to use only one of the many possible independent sets. For systems of atoms having some other symmetry than that corresponding to rotations in a plane it is advantageous to use instead of the Rumer, that independent set which most nearly possesses the symmetry of the atomic configuration. We, therefore, considered it desirable to develop some method which would make more easy the expansion of a bond eigenfunction in terms of any l.i.s. (linearly independent set).

An analytical solution of this problem is suggested when one considers the function space of higher dimensions which underlies that of the bond eigenfunctions. A bond eigenfunction ψ_j can be represented as a linear combination of the antisymmetric configuration eigenfunctions φ_i which have the same eigenvalue for S_z the total z-component of spin. The φ_i are the determinants defined by[4]

$$\varphi_i=(1/(N!)^{\frac{1}{2}})\sum_P(-1)^P P(a\alpha(1), b\beta(2), \cdots). \quad (1)$$

Here N is the number of orbitals a, b, etc.; so that $1/(N!)^{\frac{1}{2}}$ is the factor which just normalizes the $N!$ terms of (1) to the approximation of neglecting non-orthogonality of the orbitals. The quantities α and β are the two eigenfunctions for the S_z for a single electron with the corresponding eigenvalues $h/4\pi$ and $-h/4\pi$. The operation P permutes the electrons among the orbitals. Such an eigenfunction can be represented symbolically in a very simple fashion, by indicating which spin eigenfunction is associated with each orbital. Thus for the singlet state of the four electron problem we write $\begin{pmatrix} a & b & c & d \\ \alpha & \beta & \alpha & \beta \end{pmatrix}$ for the eigenfunction which has the eigenvalue $S_z=0$, and which has β's in the b and d columns of its determinant.

These φ_i's are all linearly independent, whereas the ψ's are not. Furthermore, the coefficients of the φ_i's that combine to give a ψ_j can be only ± 1

[1] Parker Fellow of Harvard University.

[2] (a) Rumer, Nach. Ges. Wiss. Gott. M. P. K. **1932**, 332; (b) Rumer, Teller and Weyl, ibid. **1932**, 499.

[3] (a) Eyring and Sun, J. Chem. Phys. **2**, 299 (1934); (b) Bear and Eyring, ibid. **3**, 98 (1935).

[4] These are simply the antisymmetrical determinants used by (a) Slater, Phys. Rev. **34**, 1293 (1929). For a more complete discussion see (b) Eyring and Kimball, J. Chem. Phys. **1**, 246 (1933); and (c) Bear and Eyring, reference 3(b).

or 0, while in the expansion of a ψ_j in terms of ψ's that are linearly independent, the coefficients are not thus restricted. Let us now suppose that we have an independent set $\psi_1, \psi_2, \cdots \psi_s$ and expand ψ_k in terms of this set.[5]

$$\psi_k = \sum_{r=1}^{s} a_{rk}\psi_r. \tag{2}$$

But we have also $\psi_k = \sum_{i=1}^{l} b_{ik}\varphi_i$ (3a)

and $\psi_r = \sum_{i=1}^{l} b_{ir}\varphi_i.$ (3b)

Therefore, substituting in (2) the expansions of ψ_k and ψ_r from (3a) and (3b) and equating the coefficients of φ_i we get

$$b_{ik} = \sum_{r=1}^{s} a_{rk}b_{ir}. \tag{4}$$

It is convenient to think of the φ's (antisymmetric configuration eigenfunctions) as constituting a set of mutually orthogonal unit vectors. The ψ's (bond eigenfunctions) are then vectors in this space with one end at the origin and the other given by adding and subtracting vectorially an equal number of these orthogonal unit vectors. The coefficient b_{ik} in (3a) is then just the scalar product $\varphi_i \cdot \psi_k$ (4a). This scalar product is not to be confused with the integral $\int \varphi_i^* \psi_k d\tau$, with which it agrees if $\int \varphi_i^* \varphi_j d\tau = \delta_{ij}$. The use of (4a) is of course not a limitation on our method of determining linear dependence.

It is clear that b_{ik} and b_{ir} can also be expressed as the simple operators $D_i = (\partial/\partial\varphi_i) = \varphi_i \cdot$, acting on ψ_k and ψ_r, respectively, whence

$$D_i\psi_k = \sum_{r=1}^{s} a_{rk} D_i\psi_r. \tag{5}$$

We evaluate $D_i\psi_r$ for our independent set and substitute in (5), which process gives l equations ($l > s$) from any s of which we can solve for the s unknowns (the a_{rk}) in terms of the $D_i\psi_k$. It is always possible to choose a set of s equations in such a way that one obtains linear equations of the form:

$$a_{rk} = (D_m + D_n + \cdots - D_p - D_q - \cdots)\psi_k. \tag{6}$$

The operator in the brackets is independent of k. We can therefore write

$$a_{rk} = A_r\psi_k, \tag{7}$$

where $A_r = (D_m + D_n + \cdots - D_p - D_q - \cdots).$ (8)

The operation A_r on ψ_k of course amounts simply to taking a sum of scalar products. We have then a convenient method of obtaining the coefficients in the expansion of *any* bond eigenfunction. We need determine only once the operator A_r for each ψ_r and then the coefficient of that ψ_r in the expansion of any ψ_k is given by A_r operating on that ψ_k. The simplest coefficients for any independent set will be found by picking the s equations properly. In the applications that follow it will be shown how easily this may be done.

II. Applications to Singlet Eigenfunctions

A. Three bonds

Let us consider in detail the resolution of six electron bond eigenfunctions for the singlet state. For this case there are twenty φ_i's and fifteen ψ_j's, of which five of the latter are linearly independent. We shall arrange the φ_i's as follows. We shall write at the top of a column $a\ b\ c\ d\ e\ f$ representing the six orbitals involved. Then we shall distribute three α's and three β's in all the twenty possible ways among these orbitals by arranging them as one would in constructing a dictionary. Thus $\varphi_1 = \begin{pmatrix} a\ b\ c\ d\ e\ f \\ \alpha\ \alpha\ \alpha\ \beta\ \beta\ \beta \end{pmatrix}$, $\varphi_2 = \begin{pmatrix} a\ b\ c\ d\ e\ f \\ \alpha\ \alpha\ \beta\ \alpha\ \beta\ \beta \end{pmatrix}$ and $\varphi_{20} = \begin{pmatrix} a\ b\ c\ d\ e\ f \\ \beta\ \beta\ \beta\ \alpha\ \alpha\ \alpha \end{pmatrix}$. When we arrange the φ_i's in this manner we see that φ_{20} through φ_{11} are the reflections of φ_1 through φ_{10}, i.e., they have α's where β's were and *vice versa*. Thus the coefficients of φ_{20} through φ_{11} in any expansion of a bond eigenfunction will be the negative of those of φ_1 through φ_{10}. Therefore in our further work we need only consider φ_1 through φ_{10}. In the expansion of any bond eigenfunction ψ_j the coefficients of the φ_i's can be determined in the following manner. Corresponding to each φ_i we define an operator D_i of the form $[def]$ in which the letters simply list the orbitals in the corresponding φ_i which are

[5] In all that follows the subscript k refers to the specific bond function in which we are interested, and does not change, while r may be any one of the s linear independent bond functions and i any one of the l Slater functions.

associated with β's. Operating on a bond eigenfunction such as $\psi_4=ab\ cd\ ef$, D_i gives 0 if any two of the orbitals occur in any one bond; otherwise it gives $+1$ if the number of letters in it which are first letters of bonds is even and -1 if this number is odd. The following convention is to be understood for the ψ's. In each bond the letter coming first in the alphabet is written first and this eigenfunction we indicate by plus ψ_k. Interchanging the order of the letters in one bond changes the sign of ψ_k.

Thus $[def]\psi_4=0$; $[bce]\psi_4=1$; $[bcf]\psi_4=-1$, etc. We consider, therefore, ten such operators, $D_1=[def]$, $D_2=[cef]$, $\cdots D_{10}=[bcd]$. For our five linearly independent ψ's let us first choose the Rumer set.

$$\begin{aligned} \psi_1&=af\ bc\ de, & \psi_4&=ab\ cd\ ef,\\ \psi_2&=ad\ bc\ ef, & \psi_5&=ab\ cf\ de.\\ \psi_3&=af\ be\ cd, \end{aligned} \tag{9}$$

Now any other eigenfunction ψ_k can be written as

$$\psi_k=a_{1k}\psi_1+a_{2k}\psi_2+a_{3k}\psi_3+a_{4k}\psi_4+a_{5k}\psi_5 \tag{10}$$

and we are interested in finding the a_{ik}'s. Operating on ψ_k with the brackets defined above we obtain:

$$\begin{aligned} d_{1k}&=[def]\psi_k=a_{3k},\\ d_{2k}&=[cef]\psi_k=a_{1k}-a_{3k},\\ d_{3k}&=[cdf]\psi_k=-a_{1k}+a_{2k},\\ d_{4k}&=[cde]\psi_k-a_{2k},\\ d_{5k}&=[bef]\psi_k=-a_{1k}+a_{5k},\\ d_{6k}&=[bdf]\psi_k=a_{1k}-a_{2k}-a_{3k}+a_{4k}-a_{5k},\\ d_{7k}&=[bde]\psi_k=a_{2k}-a_{4k},\\ d_{8k}&=[bcf]\psi_k=a_{3k}-a_{4k},\\ d_{9k}&=[bce]\psi_k=a_{4k}-a_{5k},\\ d_{10k}&=[bcd]\psi_k=a_{5k}, \end{aligned} \tag{10a}$$

where

$$d_{ik}=D_i\psi_k. \tag{10b}$$

From the five equations for d_{1k}, d_{2k}, d_{4k}, d_{9k} and d_{10k} we get the following solutions for the a's.

$$\begin{aligned} a_{1k}&=d_{1k}+d_{2k}, & a_{4k}&=d_{9k}+d_{10k},\\ a_{2k}&=-d_{4k}, & a_{5k}&=d_{10k}.\\ a_{3k}&=d_{1k}, \end{aligned} \tag{11}$$

For the expansion of any three-bond eigenfunction ψ_k in terms of the Rumer set we, therefore, have,

$$\psi_k=[\psi_1(D_1+D_2)-\psi_2D_4+\psi_3D_1 +\psi_4(D_9+D_{10})+\psi_5D_{10}]\psi_k. \tag{12}$$

It is possible to pick an independent set in which not more than one operator is required to calculate each coefficient. This can be done by letting the ten D_i's operate on all fifteen ψ's and then picking out five suitable ψ's. When this is done we find that such a set is given by $\psi_1'=ab\ cd\ ef$, $\psi_2'=af\ bc\ de$, $\psi_3'=ab\ ce\ df$, $\psi_4'=ae\ bc\ df$, $\psi_5'=af\ be\ cd$. The coefficients are $A_1'=D_9$, $A_2'=-D_3$, $A_3'=D_{10}$, $A_4'=-D_4$, $A_5'=D_1$, where A_i was defined in Eqs. (7) and (8) and D_i was defined in (10b). The expansion of any ψ_k in terms of this set then becomes

$$\psi_k=[\psi_1'D_9-\psi_2'D_3+\psi_3'D_{10} -\psi_4'D_4+\psi_5'D_1]\psi_k. \tag{13}$$

Thus we see that it is a very simple matter to expand any bond eigenfunction in terms of any complete set. Even for the Rumer set it is no longer necessary to draw diagrams and repeated superposition patterns each time an eigenfunction is expanded. Eqs. (12) or (13) need be obtained only once and then can be applied to any ψ_k.

Eq. (12) may be written in a simpler form by taking advantage of the symmetry properties of the Rumer set. The five eigenfunctions form only two patterns which can be represented by rotation (or permutation) groups of order two and three. Thus ψ_1 is carried into $-\psi_4$ by the odd permutation $R=(abcdef)$ and $-\psi_4$ into ψ_1 by repeating this permutation. The sign of an eigenfunction obtained by applying to a positive eigenfunction the permutation $(abcdef)$ p times is $(-)^p$. The same permutation changes ψ_2 into $-\psi_3$, $-\psi_3$ into ψ_5, and ψ_5 into $-\psi_2$. As stated before the operation D_i is simply $\varphi_i\cdot$, so that the odd permutation $R=(abcdef)$ applied p times gives $(-)^p\varphi_j\cdot=(-)^pD_j$.[6] Furthermore, if the operator D_j is one used to determine the coefficient of ψ_r, then $(-)^pR^pD_j$ is the operator associated with $(-)^pR^p\psi_r$. Thus we can rewrite (12) as

[6] This follows because any permutation applied to a φ_i gives some other Slater eigenfunction φ_j, and hence this permutation applied to the operator $\varphi_i\cdot$ (which symbolizes the taking of a scalar product of φ_i with the eigenfunction that is operated upon) gives the operator $(-)^P-\varphi_j\cdot$, which in our alternate notation is the operator $(-)^PD_j$. If it should so happen that the permutation carries the given operator into one belonging to the set $\varphi_{11}\cdot$ to $\varphi_{20}\cdot$ inclusive (such as $[aef]$, for example), one can either keep it or replace it by the negative of its reflection from the set $\varphi_i\cdot$ to $\varphi_{10}\cdot$ (i.e. $-[bcd]$).

$$\psi_k=\left\{\sum_{i=0}^{1}R^i[\psi_1([def]+[cef])]-\sum_{i=0}^{2}R^i(\psi_2[cde])\right\}\psi_k. \quad (14)$$

This simple way of writing the expansion does not diminish the actual labor of carrying out the operation itself but will be found very convenient for the representation of eigenfunctions of more bonds where the number of those in the l.i.s. becomes quite large. Furthermore it does reduce the amount of labor needed to determine the operators since it is now necessary to find the operator for only one bond eigenfunction of each pattern. When the Rumer set is used it is found that those operators D_i give the simplest coefficients a_{ik} which have the largest number of β's associated with neighboring orbitals (successive letters). With these simplifications it becomes possible to determine quickly the expansions for eigenfunctions of many bonds.

Another advantage of the notation employed in Eq. (14) is perceived when we proceed to determine the character of a representation. If we let some operator B act upon our independent set we get the character χ of the corresponding transformation from the equation

$$\chi=\sum_{r=1}^{s}A_rB\psi_r. \quad (15)$$

If ψ_1 to ψ_n can be obtained from ψ_1 by the permutation P^i and ψ_{n+1} to ψ_r by a permutation Q^i on ψ_{n+1} we have

$$\chi=\sum_{i=1}^{n}A_iBP^i\psi_1+\sum_{i=n+1}^{r}A_iBQ^i\psi_{n+1}. \quad (16)$$

In the particular cases for which B and P and B and Q commute it is seen that (16) can be much further simplified.

B. Four bonds

The Rumer set of four-bond eigenfunctions has fourteen members which fall into three groups of orders two, four and eight. These groups can be generated by the permutation $R=(abcdefgh)$ operating on $\psi_1=ab\ cd\ ef\ gh$; $\psi_2=ad\ bc\ eh\ fg$ and $\psi_3=ab\ cd\ eh\ fg$, respectively. The coefficients of these eigenfunctions are readily found to be

$$\begin{aligned}a_{1k}&=([bcfg]-[bcde]-[defg])\psi_k=A_1\psi_k,\\ a_{2k}&=([cdef]\psi_k=A_2\psi_k,\\ a_{3k}&=([bdef]+[cdef])\psi_k=A_3\psi_k.\end{aligned} \quad (17)$$

The eleven other coefficients are obtained from these by repeated application of the cyclic permutation R. We have then for the expansion of any four bond singlet eigenfunction in terms of the Rumer set,

$$\psi_k=\left\{\sum_{i=0}^{1}R^i(\psi_1A_1)+\sum_{i=0}^{3}R^i(\psi_2A_2)+\sum_{i=0}^{7}R^i(\psi_3A_3)\right\}\psi_k. \quad (18)$$

In the above set only four coefficients have one term, while eight have two terms and two have three terms. There exists a set for which eleven coefficients have one term, two have two terms, and one has three terms. It is the following:

$$\begin{aligned}
\psi_1&=ab\ cd\ eg\ fh, & A_1&=[bdgh],\\
\psi_2&=ab\ ce\ dg\ fh, & A_2&=[begh],\\
\psi_3&=ab\ cf\ dg\ eh, & A_3&=[bfgh],\\
\psi_4&=ac\ bd\ ef\ gh, & A_4&=[cdfh],\\
\psi_5&=ac\ be\ df\ gh, & A_5&=[cefh],\\
\psi_6&=ad\ bg\ ce\ fh, & A_6&=[degh],\\
\psi_7&=ad\ bg\ cf\ eh, & A_7&=[dfgh],\\
\psi_8&=ac\ be\ dg\ fh, & A_8&=[cegh],\\
\psi_9&=ac\ af\ bg\ eh, & A_9&=[cfgh],\\
\psi_{10}&=af\ ce\ bg\ dh, & A_{10}&=[efgh],\\
\psi_{11}&=ad\ be\ cf\ gh, & A_{11}&=[defh],\\
\psi_{12}&=ab\ ce\ df\ gh, & A_{12}&=[befh]+[efgh],\\
\psi_{13}&=ac\ bd\ eg\ fh, & A_{13}&=[cdef]-[cegh],\\
\psi_{14}&=ab\ cd\ ef\ gh, & A_{14}&=[bdeg]-[befh]-[efgh].
\end{aligned}$$

C. Five bonds

There are 42 linearly independent five-bond eigenfunctions. The members of the Rumer set, however, form only six rotation groups, one of order two, two of order five and three of order ten. These six groups can be generated by the cyclic permutation from the eigenfunctions

$$\begin{aligned}
\psi_1&=ab\ cd\ ef\ gh\ ij & &\text{(order 2)},\\
\psi_2&=ab\ cj\ di\ eh\ fg & &\text{(order 5)},\\
\psi_3&=aj\ bc\ di\ ef\ gh & &\text{(order 5)},\\
\psi_4&=ab\ cj\ di\ ef\ gh & &\text{(order 10)},\\
\psi_5&=ab\ cj\ dg\ ef\ hi & &\text{(order 10)},\\
\psi_6&=ab\ ej\ de\ fg\ hi & &\text{(order 10)}.
\end{aligned}$$

The following are the coefficients of these eigenfunctions from which the others may be gener-

ated by the cyclic permutation $R=(abcdefghij)$:

$$a_{1k}=([cdefg]+[bdefg]-[bcdef]-[bcdeg]+[bcehi]+[bedhi]+[dfghi]+[efghi])\psi_k=A_1\psi_k,$$
$$a_{2k}=[bcdef]\psi_k=A_2\psi_k,$$
$$a_{3k}=([bcdef]+[bcdeg]+[acdeg]+[acdef])\psi_k=A_3\psi_k,$$
$$a_{4k}=([bcdef]+[bcdeg])\psi_k=A_4\psi_k,$$
$$a_{5k}=([bcdef]+[bcdeg]+[bcdeh])\psi_k=A_5\psi_k,$$
$$a_{6k}=([bcdef]+[defgh]+[cefgh]-[bcdgh]+[befgh])\psi_k=A_6\psi_k.$$

D. Six bonds

There are 132 linearly independent six-bond singlet eigenfunctions. The symmetry properties of the Rumer set reduce these to 14 rotation groups, one of order 2, one of order 4, three of order 6 and eight of order 12. We shall give in some detail the method of obtaining the coefficients in this case as it throws some light on the way in which symmetry properties may be used to reduce enormously the labor of the calculation. Thus the operators for this set were obtained in several hours, whereas the method of uncrossing a single much crossed eigenfunction takes a time of an entirely different order of magnitude. Even to expand an eigenfunction by the simplified methods previously suggested[3] would take longer than this operator method since in the former method to determine each coefficient it is necessary to draw a new diagram.

Let us assume that twelve points $a, b, c \cdots, l$, representing the orbitals, are arranged in order on the circumference of a circle (8). A bond between two of the orbitals is represented by the chord connecting the two points. Following a definition of Rumer, Teller and Weyl,[2b] we shall measure the length of the arc subtended by this chord, by the number of points on the arc, the two terminal points each counting one-half. We have already noted that the simplest coefficients are given by those operators representing antisymmetric configuration eigenfunctions in which all the β's are on adjacent orbitals. We see at once that such an operator will give zero when acting on any bond eigenfunction except one of that symmetry group in which there are just two arcs of unit length. (Such an eigenfunction is *ab cl dk ej fi gh*.) The next simplest operator is that with five β's on adjacent orbitals. Such an operator will give zero when acting on all eigenfunctions except one of the symmetry group already mentioned and one of a group with just three arcs of length one. When one proceeds to choose the operators in such an orderly manner one finds that the solution of the fourteen simultaneous equations that are needed is made quite easy, since each new equation involved only the quantities that have occurred in previous equations. Thus, the fourteen eigenfunctions which follow are those of the Rumer set of 132 for which we require the corresponding operators.

	Order of rot. group
$\psi_1=ab\ cl\ dk\ ej\ fi\ gh$	6
$\psi_2=ab\ cl\ dk\ ej\ fg\ hi$	12
$\psi_3=ab\ cl\ dk\ eh\ fg\ ij$	12
$\psi_4=ab\ cl\ dk\ ef\ gj\ hi$	12
$\psi_5=ab\ cl\ dk\ ef\ gh\ ij$	12
$\psi_6=ab\ cl\ dg\ ef\ hk\ ij$	4
$\psi_7=ab\ cl\ di\ ef\ gh\ jk$	12
$\psi_8=ab\ cl\ de\ fk\ gb\ ij$	12
$\psi_9=ab\ cl\ dg\ ef\ hi\ jk$	12
$\psi_{10}=ab\ cd\ el\ fk\ gh\ ij$	6
$\psi_{11}=ab\ cl\ de\ fi\ gh\ jk$	6
$\psi_{12}=ab\ cl\ de\ fg\ hi\ jk$	12
$\psi_{13}=ab\ cd\ ej\ fg\ hi\ kl$	12
$\psi_{14}=ab\ cd\ ef\ gh\ ij\ kl$	2

The fourteen eigenfunctions given above are in the order of complexity of their operators. Thus the operator associated with ψ_1 has one term, that of ψ_2 two terms, etc. Furthermore, their symmetry relations are such that each one contains the operator associated with the eigenfunctions that have gone before. This will be made clear by the following table. In this we give the operator coefficients of the eigenfunctions (A_r), not explicitly in terms of the D_r's, but in terms of the A's of the preceding eigenfunctions and whatever other D's are necessary. In the actual expansion the labor is reduced if the coefficients are determined in this same order. This order can be followed with advantage in the cases of three, four and five-bond eigenfunctions.

In order to get these relations in the simplest form it was necessary to use besides the operators for the fourteen eigenfunctions given above some of the others which are obtained by the repeated cyclic permutation. Thus in the expression for A_9 the symbol R^4A_3 means that one repeats four times the permutation $R=(abcdefghijkl)$ on A_3. The expression R^4A_3 is the operator associated with the eigenfunction $R^4\psi_3$, which is *ab ch dg ef il jk*.

$$A_1=[bcdefg],$$
$$A_2=[bcdefh]+A_1,$$
$$A_3=[bcdefi]+A_2,$$
$$A_4=[bcdegh]+A_2,$$
$$A_5=[bcdegi]-A_2,$$
$$A_6=[bcdehi]+A_5,$$
$$A_7=[bcdegj]-[bcdefj]+A_5,$$
$$A_8=[bcdfgi]-[bcdfgh]+A_5,$$
$$A_9=[bcdeij]+A_4+R^4A_3,$$
$$A_{10}=[bcefhi]+A_8+R^8A_7-R^8A_9,$$
$$A_{11}=[bcdfgj]+A_1-A_5+A_7+A_8,$$
$$A_{12}=[bcdghj]+[aefjkl]+R^4A_7+A_2+R^6A_4,$$
$$A_{13}=[bcgijk-A_1+A_2+R^6A_5-R^2A_6+R^{10}A_9,$$
$$A_{14}=[bcfgjk]-A_1-R^2A_1+A_5+R^2A_5$$
$$+R^4A_5+R^6A_5+R^8A_5+R^{10}A_5-A_6-R^2A_6.$$

III. The Expansion of Bond Eigenfunctions of Higher Multiplicities

The resolution of bond eigenfunctions of higher multiplicity could also be carried through by this same method of operators. However, for high multiplicities the number of linearly independent bond eigenfunctions becomes so large that the method begins to become unwieldy. For such cases one may use to advantage a combination of the geometric and analytic methods. The l.i.s. for higher multiplicities may be obtained in the following way.[2b] The n orbitals a_1 to a_n are arranged in order on a circle. Since we are concerned with higher multiplicities, not all of these orbitals are bound to others. A reference orbital is inserted on the circumference between a_1 and a_n. The independent set is that one composed of eigenfunctions in which no lines cross, when, beside the lines representing actual bonds, one adds additional straight lines connecting the unbound orbitals with the reference orbital.

The first step in the resolution of bond eigenfunctions of higher multiplicities is to disregard all orbitals that are not connected by bonds and to expand the resulting eigenfunction in terms of an uncrossed set by the methods of the preceding section for the singlet state. These resulting uncrossed eigenfunctions will not in general be members of the l.i.s. We must, then, expand each of them.

It has been shown[7] that there is a vector-like relationship between eigenfunctions which are exactly the same except for a single bond. If these differing bonds when superposed on the same circle form a closed polygon any one of the eigenfunctions can be represented as the vector sum of the rest. This principle, together with the definition of a l.i.s. given above, enables us to expand our uncrossed eigenfunction in terms of the l.i.s.

The method of expanding an eigenfunction of any number of bonds and of any multiplicity is now summarized. After one has applied to a crossed eigenfunction the method for obtaining an uncrossed set, as previously described, each one of the set is separately expanded. First we introduce some definitions. We speak of the bond which has one of its ends farthest from our reference orbital as B_0 the one next to it as B_1, etc. By the arc subtended by B_1 is meant the arc which does not contain the reference orbital. We next define a quantity which we will call the weight of a bond. The weight of B_0 is equal to the length of its arc n_0 (defined previously). The weight of B_i is its length minus $2i$. The product of the weights for all bonds of an eigenfunction ψ gives the number of eigenfunctions of the l.i.s., which will occur in the expansion of ψ. If for every eigenfunction the orbital in a bond with the lower ordinal number is written first all these eigenfunctions will occur with a coefficient $+1$. This is the convention of sign which has been employed throughout the paper.

To resolve the eigenfunction ψ one first expresses it as the sum of eigenfunctions which differ from ψ only in having B_0 replaced in turn by each possible bond B_0' lying along the arc subtended by B_0. Each of the resulting new functions is in turn replaced by a sum. This sum is obtained by replacing B_1, successively, by all the bonds which add vectorially to give B_1 and which follow along the arc of B_1 at all points except at the two points corresponding to the extremities of the B_0' for this eigenfunction. These points are omitted. This same process is continued for all the bonds up to B_{n-1} (there being assumed to be n bonds). In expanding a particular eigenfunction by successive replacements of the bond B_i we proceed as for B_1 except that we now omit the $2i$ points on the arc of B_i which coincide with the two extremities of the i bonds $B_0'B_1'\cdots B'_{i-1}$. Thus eigenfunctions for higher multiplicities, for any number of bonds n, are readily resolved in terms of the linear independent set.

[7] Eyring, Frost and Turkevich, J. Chem. Phys. **1**, 777 (1933).

The Quantum-Mechanical Treatment of Molecules by the Method of Spin Valence*

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The method of spin valence, developed by Born, Heitler, Rumer and Weyl for the treatment of molecular systems, becomes completely equivalent to the Slater method if the bonding forces are considered to be exerted between individual orbitals, and not between entire atoms in definite spectroscopic states. This change in the point of view eliminates several difficulties which were formerly present in the method (e.g., the obscuring of the directional properties of the valence bonds). The secular equation, for which a simplified derivation is given, is of quite a different form from the Slater equation, and the problem of its solution is considered in some detail. In addition to the rigorous methods, several approximate methods are given, of which two (applicable to unsaturated and aromatic hydrocarbons) do not require that the secular equation be set up at all. The method of spin valence is found to be more convenient than the Slater method for the treatment of systems of high multiplicity. Finally, the extension to cases of orbital, as well as spin degeneracy is briefly outlined.

INTRODUCTION

THE method outlined by Slater[1] for the quantum-mechanical treatment of molecular structure is of such general applicability that certain other procedures which have been devised and which lead to the same final result are apt to be completely neglected. (I am not concerned here with the method[2] associated chiefly with the names of Hund and of Mulliken, since this starts from an essentially different basis and is not strictly comparable with Slater's treatment.) Van Vleck and Serber,[3] to be sure, have recently pointed out that the Dirac vector model is quite useful for many purposes, but very little attention seems to have ever been paid to the so-called method of spin valence developed by Born, Heitler, Rumer and Weyl.[4] One reason for this neglect is probably to be found in the fact that, in its usual formulation, the method treats only the interactions between entire atoms in definite spectroscopic states, and not those between the individual electrons. This makes it almost necessary to assume each atom to be in an S state, and obscures the directional properties of the valence bonds to such an extent as to invalidate many of the conclusions reached. The incorrect result obtained by Markov,[5] for example, that benzene should be less stable than three acetylene molecules is apparently to be explained on this basis. This difficulty, however, is not at all essential, and, as we shall see immediately, can easily be avoided.

In the following development, a method of attack will be adopted which differs from that usually employed in that it assumes the Slater valence-bond functions at the outset. This eliminates at once the above-mentioned difficulty, and simplifies the subsequent treatment by rendering unnecessary any recourse to the unfamiliar theory of the invariants of binary forms. With this alteration, the method of spin valence becomes completely equivalent to the ordinary Slater treatment, although it remains quite different in form. It always leads to the same answer as the latter in any definite problem, but it frequently allows the calculation to be made with the expenditure of considerably less time and labor. Even in the cases in which it offers no special advantages, it is still useful in that it furnishes an independent check upon the results obtained in other ways.

OUTLINE OF THE METHOD

For the present, the discussion will be limited to problems of spin degeneracy only, and to systems in singlet states. If we have $2N$ orbitals, $a, b, \cdots y, z$, each occupied by one electron, we

* No. 455.

[1] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[2] F. Hund, Zeits. f. Physik **73**, 1 (1931); **73**, 565 (1932). R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933) and further references given there. Cf. also E. Hückel, Zeits. f. Physik **72**, 310 (1931); **76**, 628 (1932); **83**, 632 (1933).

[3] J. H. Van Vleck, Phys. Rev. **45**, 405 (1934). R. Serber, Phys. Rev. **45**, 461 (1934); J. Chem. Phys. **2**, 697 (1934).

[4] M. Born, Zeits. f. Physik **64**, 729 (1930); Ergebnisse d. Exakt. Naturwissenschaften, X 387 (1931). W. Heitler and G. Rumer, Zeits. f. Physik **68**, 12 (1931); H. Weyl, Nach. Ges. Wiss. Gött., M. P. Klasse, **1930**, 285; **1931**, 33; G. Rumer, ibid. **1932**, 337.

[5] M. Markov, J. Chem. Phys. **1**, 784 (1933).

can set up a Slater function for each possible way of drawing valence bonds. For bonds between a and b, c and d, $\cdots y$ and z, for example, we have[6]

$$\Psi=\frac{1}{(2^N(2N)!)^{\frac{1}{2}}}\sum_k(-1)^kR_k\sum_j(-1)^jP_j \times\{a(1)\alpha(1)b(2)\beta(2)\cdots y(2N-1) \times\alpha(2N-1)z(2N)\beta(2N)\}, \quad (1)$$

where P_j is one of the $(2N)!$ operations of permuting the electrons among the orbital and spin functions, and R_k is one of the 2^N operations of interchanging the spins associated with the orbitals involved in one or more bonds. P_j is an even, or an odd, permutation when j is even, or odd, respectively; and R_k corresponds to an even, or to an odd, number of interchanges when k is even, or odd, respectively. In order to avoid confusion in regard to the sign of the function, we shall adopt the following convention: Let each valence bond in the structure be represented by an arrow. Then the corresponding function is

$$\Psi=\frac{1}{(2^N(2N)!)^{\frac{1}{2}}}\sum_k(-1)^kR_k\sum_j(-1)^jP_j \times\{a(1)\sigma_a(1)b(2)\sigma_b(2)\cdots z(2N)\sigma_z(2N)\}, \quad (2)$$

where

$$\sigma_r=\begin{cases}\alpha, \text{ if the orbital } r \text{ is at the tail of an arrow}\\ \beta, \text{ if the orbital } r \text{ is at the head of an arrow.}\end{cases}$$

In that term of the double summation for which R_k and P_j are both equal to the identity operator I, the orbitals follow in alphabetical, and the electrons in numerical order. Reversing an arrow in the structure then changes the sign of the corresponding function. In the structure represented by Eq. (1), for example, the arrows point from a to b, $\cdots$, from y to z.

If the summation over k is actually performed, Eq. (1) becomes

$$\Psi=\frac{1}{(2^N(2N)!)^{\frac{1}{2}}}\sum_j(-1)^jP_j\{a(1)b(2)\cdots z(2N)[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\cdots \times[\alpha(2N-1)\beta(2N)-\beta(2N-1)\alpha(2N)]\}$$

$$=\frac{1}{(2^N(2N)!)^{\frac{1}{2}}}\sum_j(-1)^j(P_ju)(P_j\varphi) \quad (3)$$

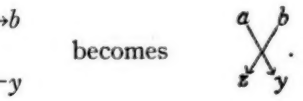
where, for convenience, we have set

$$u=a(1)b(2)\cdots z(2N)$$

and

$$\varphi=[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\cdots \times[\alpha(2N-1)\beta(2N)-\beta(2N-1)\alpha(2N)].$$

From this original structure, any other that may be desired can be obtained by redirecting the arrows in a suitable manner. Such a redirection can be represented by a permutation, T_i, acting upon the orbitals. If, for example, T_i is the simple interchange (by), the corresponding structure is that in which the arrow, which formerly had its head (or tail) at b, now has its head (or tail) at y, and *vice versa*. That is,

$a\rightarrow b$ becomes  .

$z\leftarrow y$

Any other bonds (such as between c and d, etc.) remain unchanged. It is readily seen that the function which represents this new structure is

$$\Psi_i=\frac{(-1)^i}{(2^N(2N)!)^{\frac{1}{2}}}\sum_j(-1)^j(P_jT_iu)(P_j\varphi). \quad (4)$$

The factor $(-1)^i$ ensures that the direction of each arrow in the vector-bond structure will remain unchanged in the course of the permutation.

We can put Eq. (4) into a more convenient form by noting that T_i can be replaced by P_i^{-1}, where P_i is the same permutation of the electrons, 1, 2, $\cdots 2N$, as T_i is of the orbitals, a, b, $\cdots z$. This gives

$$\Psi_i=\frac{1}{(2^N(2N)!)^{\frac{1}{2}}}\sum_j(-1)^{j+i}(P_jP_i^{-1}u)(P_j\varphi). \quad (5)$$

If now we denote $P_jP_i^{-1}$ by $P_{j'}$, we have, since P_i and P_i^{-1} are even or odd simultaneously,

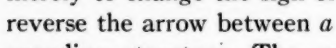
$$\Psi_i=\frac{1}{(2^N(2N)!)^{\frac{1}{2}}}\sum_{j'}(-1)^{j'}(P_{j'}u)(P_{j'}P_i\varphi),$$

or, dropping the primes and setting $P_i\varphi=\varphi_i$

[6] The first explicit statement of this rule (in a slightly different, but equivalent form) seems to have been made by G. E. Kimball and H. Eyring, J. Am. Chem. Soc. **54**, 3876 (1932).

$$\Psi_i=\frac{1}{(2^N(2N)!)^{\frac{1}{2}}}\sum_j(-1)^j(P_ju)(P_j\varphi_i). \quad (6)$$

There are $(2N)!$ permutations T_i and hence $(2N)!$ functions Ψ_i which can be obtained in this way, but of these only $(2N)!/[N!(N+1)!]=p_N$ can be independent, since there are only p_N singlet states. It is obvious, for example, that if T_i is the interchange (ab) in Eq. (4), the effect is merely to change the sign of the function, or to reverse the arrow between a and b in the corresponding structure. The general case can be described in the following manner. Arrange the orbitals formally in a circle. (This need have no relation to the actual arrangement in space.) Now draw all possible structures in which each bond lies wholly within the circle, and in which no two bonds intersect. For this purpose structures which differ only in the direction of one or more of the arrows are not to be considered as distinct. There will be exactly p_N such structures, and the corresponding functions will form a complete and independent "canonical" set. Structures which contain crossed bonds can always be resolved into linear combinations of the canonical structures by repeated application of the rule[7]



or by the procedure given by Eyring and Sun.[8]

In general no single function Ψ_i will be a satisfactory representation of the molecule, and it is necessary to use a linear combination

$$\chi=\sum_{i=1}^{p_N}a_i\Psi_i \quad (7)$$

in which the a_i's are constants which are to be so chosen that χ is the best possible approximation. Instead of using the variational method, which leads to Slater's secular equation, we shall evaluate the coefficients by the ordinary first order perturbation theory. Thus, we set

$$(H-W)\chi=\sum_{i=1}^{p_N}a_i(H-W)\Psi_i=0. \quad (8)$$

If we should multiply Eq. (8) by Ψ_l $(l=1, 2, \cdots p_N)$ and integrate over all coordinates, we would again end up with Slater's secular equation. In the present treatment, however, we multiply by u, and integrate only over the spatial coordinates. In this way we obtain:

$$\sum_{i=1}^{p_N}a_i(u|H-W|\Psi_i)=\frac{1}{(2^N(2N)!)^{\frac{1}{2}}}\sum_{i=1}^{p_N}\sum_j a_i(-1)^j \times(u|H-W|P_ju)P_j\varphi_i=0,$$

or if we set

$$G_j=(-1)^j(u/H-W/P_ju)$$

and

$$P_j\varphi_i=\sum_{l=1}^{p_N}b_{il}{}^{(j)}\varphi_l,$$

we have

$$\sum_{i=1}^{p_N}\sum_{l=1}^{p_N}\sum_j a_iG_jb_{il}{}^{(j)}\varphi_l=0.$$

The φ_l's are linearly independent, and consequently the coefficient of each must vanish separately. Thus

$$\sum_{i=1}^{p_N}[\sum_j G_jb_{il}{}^{(j)}]a_i=0, \qquad (l=1, 2, \cdots p_N). \quad (9)$$

This set of simultaneous homogeneous linear equations for the a_i's has a solution if and only if the determinant of the coefficients vanishes:

$$\begin{vmatrix}\sum_j G_jb_{11}{}^{(j)} & \cdots & \sum_j G_jb_{1p_N}{}^{(j)}\\ \vdots & & \vdots\\ \sum_j G_jb_{p_N1}{}^{(j)} & \cdots & \sum_j G_jb_{p_Np_N}{}^{(j)}\end{vmatrix}=0. \quad (10)$$

This secular equation is quite different in form from the Slater secular equation which it replaces, and its matrix elements are obtained in quite a different way, but it clearly must lead to the same values of the energy W, and of the coefficients a_i. It is particularly to be noticed that the determinant is not in general symmetrical about the main diagonal, since $\sum_j G_jb_{il}{}^{(j)}$ is not necessarily equal to $\sum_j G_jb_{li}{}^{(j)}$.

An Example

In order to illustrate the method, let us consider benzene, which has already been treated by Hückel,[9] and by Pauling and Wheland.[10] We shall take into account only the interactions between the six $[p]_h$ orbitals (using Hückel's

[7] G. Rumer, Nach. Ges. Wiss. Gött., M. P. Klasse, **1932**, 337.

[8] H. Eyring and C. E. Sun, J. Chem. Phys. **2**, 299 (1934).

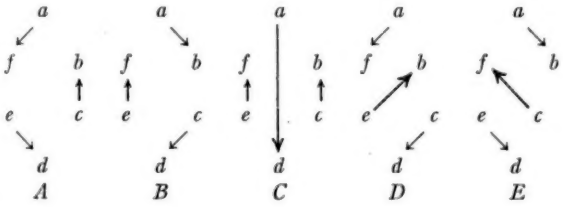
[9] E. Hückel, Zeits. f. Physik **70**, 204 (1931).

[10] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).

TABLE I.

s \ T_j	I	(ab)	(bc)	(cd)	(de)	(ef)	(fa)	Σ
A	A	$-E+A$	$-A$	$-D+A$	$-A$	$-C+A$	$-A$	$A(Q-W)+(C+D+E)\alpha$
B	B	$-B$	$-C+B$	$-B$	$-E+B$	$-B$	$-D+B$	$B(Q-W)+(C+D+E)\alpha$
C	C	$-B+C$	$-C$	$-B+C$	$-A+C$	$-C$	$-A+C$	$C(Q-W-2\alpha)+2(A+B)\alpha$
D	D	$-B+D$	$-A+D$	$-D$	$-A+D$	$-B+D$	$-D$	$D(Q-W-2\alpha)+2(A+B)\alpha$
E	E	$-E$	$-A+E$	$-B+E$	$-E$	$-B+E$	$-A+E$	$E(Q-W-2\alpha)+2(A+B)\alpha$

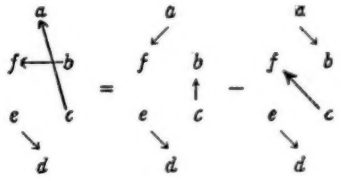
nomenclature) and we shall make the usual assumption that $G_j=Q-W$ if T_j is the identical permutation I, $G_j=-\alpha$ if T_j is a single interchange between adjacent orbitals, and $G_j=0$ otherwise. There are five canonical structures,



The actual calculation is given in Table I. At the top are listed the permutations considered (that is, those for which $G_j\neq 0$), and on the left are listed the independent spin functions. For convenience, φ_A is written simply A, and so on. The Slater function which represents the structure A, for example, is of course

$$\Psi_A=\frac{1}{24(10)^{\frac{1}{2}}}\sum_j(-1)^j(P_j u)(P_j\varphi_A).$$

In each square of the body of the table is given $P_j\varphi_i$ corresponding to the permutation T_j above and to the spin function φ_i at the left. As an illustration, the permutation $T_j=(ab)$ transforms the structure A into



Thus, $T_jA=A-E$, and, consequently, $P_j\varphi_A=\varphi_A-\varphi_E$. In the column at the extreme right of the table are the values of

$$\sum_j G_jP_j\varphi_i=\sum_j\sum_{l=A}^{E}G_jb_{il}{}^{(j)}\varphi_l$$

obtained by summing the corresponding row. From these entries the secular equation can be written down at once:

$$\begin{vmatrix} Q-W & 0 & \alpha & \alpha & \alpha \\ 0 & Q-W & \alpha & \alpha & \alpha \\ 2\alpha & 2\alpha & Q-W-2\alpha & 0 & 0 \\ 2\alpha & 2\alpha & 0 & Q-W-2\alpha & 0 \\ 2\alpha & 2\alpha & 0 & 0 & Q-W-2\alpha \end{vmatrix}=0. \tag{11}$$

This gives $W=Q-2\alpha$, $Q-2\alpha$, Q, $Q-(13^{\frac{1}{2}}+1)\alpha$, $Q+(13^{\frac{1}{2}}-1)\alpha$, and consequently the roots are exactly the same as those found by Pauling and Wheland from the Slater secular equation, and by Hückel by a much more complicated procedure.

The eigenfunction corresponding to the lowest root, $W=Q+(13^{\frac{1}{2}}-1)\alpha$, is before normalization $\Psi_A+\Psi_B+0.4341(\Psi_C+\Psi_D+\Psi_E)$. This is again the same result as was obtained by Pauling and Wheland.

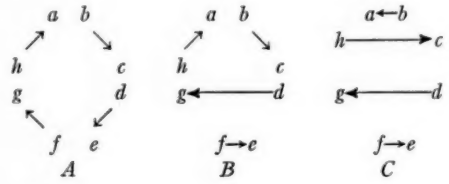
Use of Symmetry of the Molecule in Simplifying the Treatment

The calculation as carried out above is of about the same difficulty as that by the Slater treatment, but it can be greatly simplified if the energy of only the lowest state is desired. This follows from the fact that the degree of the secular equation can be reduced by taking advantage of the symmetry of the molecule.[11] It is obvious, for example, that the structures A and B must enter the complete eigenfunction for the ground state with the same coefficient, and that C, D and E must do likewise. (In order for this statement to hold, it is necessary that each arrow in each structure point from an odd numbered to an even numbered orbital, the orbitals being numbered in sequence around the circle in either direction. The starting point for the enumeration is arbitrary, but must be the same for all structures. The purpose of this convention is to ensure that the integral $(\Psi_i\Psi_j)>0$ for all i and j.) There are thus only two independent coefficients, and in consequence the secular equation can be made a quadratic. It is not necessary, however, to set up the original fifth degree equation at all, since it is possible to obtain the quadratic in one step. The procedure in the general case is as follows: Let there be several different types of structure, of which characteristic representatives are A, B, $\cdots F$, respectively, and let there be g_A structures of type A, all with coefficient a_A, g_B structures of type B, all with coefficient a_B, and so on. Of course $g_A+g_B+\cdots+g_F=p_N$, the total number of independent spin functions. Now, using only the structures A, B, $\cdots F$ as a basis, construct a table similar to Table I. If the carrying out of a permutation upon a given member of the set A, B, $\cdots F$ leads to a structure not a member of the set, this latter is represented in the table by that member of the set which belongs to the same type. The secular equation is then written down from the table in the same manner as before. If the coefficients a_A, a_B, $\cdots a_F$ are desired, they can be obtained from the equations

$$\sum_{R=A}^{F}(M_{RS}-\delta_{RS}W)a_Rg_R=0,\ (S=A,B,\cdots F),\quad(12)$$

where $M_{RS}-\delta_{RS}W$ is the RS element of the secular equation. These equations take the place of (9), from which they can be readily derived by equating all the a_i's that should be equal, and by then adding together the equations for which l refers to structures of the same type.

As an application of this procedure, we shall consider cyclooctatetrane, which has already been treated by Penney[12] by the Slater method. There are 8 electrons and hence 14 canonical structures, of which 2 are of type A below, 8 of type B, and 4 of type C. The remaining structures of each type are obtained from the characteristic example by rotation about the eightfold axis.



The results of the different permutations are given in Table II. It is understood of course that the entry corresponding to $T_j=(de)$ and $\varphi_i=C$, for example, does not mean that the result of the

[11] This is a special case of quite general group theoretical considerations. Cf. H. Eyring, A. A. Frost and J. Turkevich, J. Chem. Phys. **1**, 777 (1933); A. E. Stearn, C. H. Lindsley and H. Eyring, ibid. **2**, 410 (1934).

[12] W. G. Penney, Proc. Roy. Soc. **A146**, 223 (1934).

Table II.

φ \ T_j	I	(ab)	(bc)	(cd)	(de)	(ef)	(fg)	(gh)	(ha)	Σ
A	A	$-B+A$	$-A$	$-B+A$	$-A$	$-B+A$	$-A$	$-B+A$	$-A$	$A(Q-W)+4B\alpha$
B	B	$-C+B$	$-B$	$-B+B$	$-A+B$	$-B$	$-A+B$	$-B+B$	$-B$	$B(Q-W)+(2A+C)\alpha$
C	C	$-C$	$-B+C$	$-A+C$	$-B+C$	$-C$	$-B+C$	$-A+C$	$-B+C$	$C(Q-W-4\alpha)$ $+(2A+4B)\alpha$

permutation (de) upon C is actually equal to $-B+C$, but merely that it is equal to $-$(a structure of type B)$+$(a structure of type C). The secular equation is now

$$\begin{vmatrix} Q-W & 4\alpha & 0 \\ 2\alpha & Q-W & \alpha \\ 2\alpha & 4\alpha & Q-W-4\alpha \end{vmatrix} = (Q-W)^3-4(Q-W)^2\alpha -12(Q-W)\alpha^2+40\alpha^3=0.$$

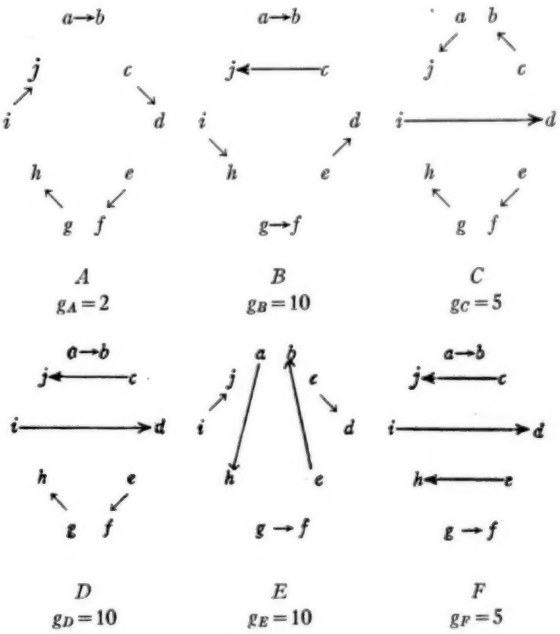
This gives $W=Q+3.3022\alpha$ for the lowest root, in complete agreement with the value found by Penney. The work involved here is much less than by the Slater treatment, which necessitates actually setting up the entire fourteenth degree equation, and then reducing it to a cubic.

Approximate Solution of the Secular Equation

First method

For still more complicated molecules, the secular equation becomes of unmanageably high degree, even after all the reduction arising from symmetry has been taken into account. In such cases it is desirable to have some method of approximation. In the Slater treatment this is quite easy, since one has only to equate the coefficients of all the first excited structures, those of all the second excited structures, and so on. One can furthermore entirely neglect the very highly excited structures since these have but little effect upon the total energy. Sherman has shown[13] by a detailed discussion of naphthalene that this procedure results in only a small error, and is a very good approximation indeed. In the present treatment, however, the secular equation is of quite a different form. In particular, it is not symmetrical about the main diagonal, and, as a consequence, the sign of the error which is introduced by the various approximations cannot be known beforehand with any certainty. Furthermore, the precise significance of the energy value obtained when the equation is not solved rigorously is no longer clear. Consequently, we cannot be sure, without further discussion, that the same approximate procedure as was used with the Slater equation will be legitimate here, but we can apply it, nevertheless, to several problems, and see how well it works in practice. This will give only an empirical check upon the method; but a rigorous theoretical treatment would be quite difficult.

As a first example, let us consider cyclodecapentane. With 10 electrons there are 42 canonical structures, which belong to the 6 types



The secular equation is found in the usual manner to be:

$$\begin{vmatrix} Q-W & 5\alpha & 0 & 0 & 0 & 0 \\ 2\alpha & Q-W-2\alpha & 2\alpha & 0 & 2\alpha & 0 \\ 0 & 4\alpha & Q-W-2\alpha & 2\alpha & 0 & 0 \\ 2\alpha & 0 & 2\alpha & Q-W-4\alpha & 2\alpha & \alpha \\ 0 & 5\alpha & 0 & 2\alpha & Q-W-4\alpha & 0 \\ 0 & 4\alpha & 0 & 4\alpha & 0 & Q-W-6\alpha \end{vmatrix} = 0. \qquad (13)$$

[13] J. Sherman, J. Chem. Phys. **2**, 488 (1934).

This equation, being of the sixth degree, is still not too complicated to be treated rigorously. On multiplying out the determinant, we obtain

$$(Q-W)^6-18(Q-W)^5\alpha+84(Q-W)^4\alpha^2 +104(Q-W)^3\alpha^3-1520(Q-W)^2\alpha^4 +3104(Q-W)\alpha^5-1600\alpha^6=0$$

of which the lowest root is $W=Q+4.031\alpha$. The correct value will serve as a useful check upon the approximate treatment, which we now apply.

Before we can do this, however, we need to observe that while the secular equation enters the calculation as the condition of compatibility of the set of Eqs. (12) for the $a_R g_R$'s, it can also be considered as the condition of compatibility of a different set

$$\sum_{S=A}^{F}(M_{RS}-W\delta_{RS})c_S=0 \quad (R=A, B, \cdots F). \quad (14)$$

In the Slater treatment, the constants c_S are just equal to the corresponding a_S's, since the secular equation is symmetrical, but in the present treatment, this is not necessarily true. The c's here are in general quite complicated functions of the a's, and their precise significance is not at all clear. Consequently we have no intuitive reason (as we do in the case of the a's) to believe that the c's for structures of the same degree of excitation should be approximately equal to each other. We assume, however, that they are, and check the legitimacy of the assumption by comparing the result thus obtained with the rigorous solution. We are justified in doing so, since the present approximate treatment is almost entirely empirical and exploratory in nature.

The procedure now is first to multiply each row of the secular equation by the corresponding g_R value,[14] and then to add the rows and columns which refer to structures whose coefficients are to be equated. Thus the Eq. (13) becomes

$$\begin{vmatrix} 2(Q-W) & 10\alpha & 0 & 0 \\ 20\alpha & 15(Q-W)+10\alpha & 30\alpha & 0 \\ 20\alpha & 70\alpha & 20(Q-W)-40\alpha & 10\alpha \\ 0 & 20\alpha & 20\alpha & 5(Q-W)-30\alpha \end{vmatrix}=0 \quad (15)$$

when we group together the first excited structures B and C, and the second excited structures D and E. On multiplying out the determinant, we find

$$100[3(Q-W)^4+22(Q-W)^3\alpha-27(Q-W)^2\alpha^2 -348(Q-W)\alpha^3-380\alpha^4]=0$$

or $W=Q+4.022\alpha$, for the lowest root. This value is in error by only 0.009α, and consequently is very good. If now we introduce the further simplification of neglecting the third excited structure F, we have merely to solve the cubic equation obtained by dropping the fourth row and column from (15). This leads to an energy of $W=Q+3.954\alpha$, in error by 0.077α, which is still fairly satisfactory. If, however, the second excited structures, D and E, are neglected as well, the energy obtained from the resulting quadratic equation is only $W=Q+2.937\alpha$; and if all excited structures are neglected, the energy is simply $W=Q$. Thus the neglect of the highly excited structures is not as satisfactory here as in the Slater treatment, and must be employed with considerable caution.

These same general conclusions are reached in a consideration of naphthalene. Here there are again 10 electrons and 42 canonical structures, but the symmetry of the molecule allows the reduction of the secular equation to be carried only as far as the sixteenth degree. Sherman[13] has given a complete treatment of this problem by the Slater method, and has shown that the rigorous solution is $W=Q+4.0400\alpha$. We shall not solve the present equation rigorously,[15] but shall reduce it to the fifth degree by equating the coefficients of the first excited structures, those of the second, and those of the third. This gives

[14] The purpose of this step is to ensure that the subsequent adding of rows will equate the coefficients a_R, and not the products $a_R g_R$.

[15] Dr. J. Sherman and the author, however, have proved that it is completely equivalent to the Slater equation. The proof rests upon the fact that it can be made identical with the latter by the use of the familiar transformations

$$\begin{vmatrix} Q-W-\alpha & 0 & 6\alpha & 0 & 0 \\ 0 & 2(Q-W)-2\alpha & 12\alpha & 0 & 0 \\ 14\alpha & 20\alpha & 16(Q-W)-10\alpha & 38\alpha & 2\alpha \\ 8\alpha & 12\alpha & 72\alpha & 19(Q-W)-47\alpha & 12\alpha \\ 4\alpha & 8\alpha & -4\alpha & 20\alpha & 4(Q-W)-20\alpha \end{vmatrix} = 0.$$

(The same energy would be obtained if this equation were reduced still further to the fourth degree, by grouping the two different types of unexcited structures; i.e., by adding the first two rows and columns.) The lowest root is found to be $W=Q+4.0241\alpha$, in error by only 0.0159α. This is somewhat better than the value of $W=Q+4.0175\alpha$ which Sherman obtained by applying the same approximate treatment to his Slater-type equation. The neglect of the third excited structures leads to an energy of $W=Q+3.7231\alpha$, which is to be compared with the value of $W=Q+4.0172\alpha$, obtained by Sherman with the same assumption. Again we see that this latter approximation is not very satisfactory in the present method.

Second method

It is readily seen by comparing (12) and (14) that the equation

$$\sum_R \sum_S a_R g_R (M_{RS} - \delta_{RS} W) c_S = 0 \qquad (16)$$

is rigorously true for any arbitrary choice of the constants c_S if the a's are correct, and for any arbitrary choice of the constants a_R if the c's are correct. Consequently, it must be very nearly true if both the a's and the c's are approximately correct. Rough values of the various coefficients can be obtained for this purpose most easily by the method of successive approximations. That is, we first arbitrarily insert in the Eqs. (12)—or (14)—any values of the a's—or of the c's—that may seem reasonable. In this way, we obtain a set of linear equations for W, the roots of which will not be mutually consistent unless the assumed values of the coefficients are accidentally correct. We then proceed systematically to improve the consistency by varying the coefficients one or two at a time. With a little practice, this becomes quite a simple operation, and no great labor is required to obtain fairly satisfactory values. For example, in the case of cyclodecapentane, we find very easily that

$$a_A:a_B:a_C:a_D:a_E:a_F \cong 1:1/3:1/4:1/15:1/10:1/80,$$

and

$$c_A:c_B:c_C:c_D:c_E:c_F \cong 1:4/5:4/5:18/25:18/25:3/5.$$

When these values are inserted into Eq. (16), the resulting energy, $W=Q+4.037\alpha$, is in error by only 0.006α.

Further Approximate Methods Applicable to Unsaturated and Aromatic Hydrocarbons

If no great accuracy is desired, this last procedure can be made into a very simple one by the use of merely estimated coefficients. A fairly satisfactory empirical rule for doing this with the hydrocarbon molecules is as follows: Let $a=c=1$ for all unexcited structures; $a=3/10$ and $c=5/6$ for all first excited structures; $a=(3/10)^2$ and $c=(5/6)^2$ for all second excited structures; and so on.* The sort of results that can be obtained by this method is indicated in Table III (third column from the left).

A still rougher approximation consists in letting all the c's be equal to unity. Then Eq. (16) becomes

$$\sum_R \sum_S a_R g_R (M_{RS} - \delta_{RS} W) = 0$$

or

$$W = \sum_R \sum_S a_R g_R M_{RS} / \sum_R a_R g_R. \qquad (17)$$

Now, if we examine the various secular equations which have been set up above, we notice a very striking regularity, namely, that in all cases

of determinants (i.e., adding columns, etc.). This gives a practically complete check upon both equations.

* *Note added in proof:* Further investigation has shown that this rule is greatly oversimplified. The author expects to discuss the problem in further detail in a l ater paper.

TABLE III. *Approximate energies of unsaturated and aromatic hydrocarbons.*

Compound	Correct[a]	Energy Approximate I[c]	II[d]	III[e]
Benzene	$Q+2.61\alpha$	$Q+2.58\alpha$	$Q+2.68\alpha$	$Q+2.5\alpha$
Cyclooctatetrane	3.30α	3.31α	3.34α	3.3α
Cyclodecapentane	4.03α	4.03α	4.00α	4.2α
Naphthalene	4.04α	4.02α	4.11α	4.0α
Butadiene	1.73α	1.75α	α	1.8α
Hexatriene	2.48α[b]	2.54α	α	2.7α
Octatetrane	3.2α[b]		α	3.5α
Phenylethylene	3.3α[b]		3.35α	3.3α
Diphenylethylene	5.6α[b]			5.7α
Triphenylethylene	7.8α[b]			8.0α
Tetraphenylethylene	10.1α[b]			10.3α
Biphenyl	4.9α[b]		4.8α	4.8α
Diphenylbenzene	7.1α[b]			7.2α
Triphenylbenzene	9.3α[b]			9.5α

[a] L. Pauling and J. Sherman, J. Chem. Phys. 1, 679 (1933).
[b] These values were obtained by the Slater method, with only unexcited and first excited structures taken into consideration. Consequently the coefficients of α appearing here are lower limits of the true values.
[c] Values in this column were obtained from Eq. (16) with the use of estimated coefficients: $a=(0.3)^i$ and $c=(5/6)^i$ for all ith excited structures.
[d] Values in this column were obtained from Eq. (19) with a's estimated as in column I.
[e] Values in this column were obtained from Eq. (21).

$$\sum_S M_{RS}=Q+n_R, \tag{18}$$

where n_R is the number of strong bonds between adjacent orbitals in the structure R. That is, $n_R=N$ for the unexcited structures, $n_R=N-1$ for the first excited structures, and so on. This rule is easily shown to be quite general, as long as the only interchanges to be considered are those between odd numbered and even numbered orbitals, the enumeration being carried out as described above. (page 234.) (In the type of problem under consideration, this is equivalent to the restriction that only interchanges between adjacent orbitals be considered, and that the molecule contain no odd-membered rings.) Thus, putting Eq. (18) into (17), we find

$$W=Q+\sum_R a_R g_R n_R/\sum_R a_R g_R. \tag{19}$$

This relation makes it possible to calculate the approximate energy of the molecule *without setting up the secular equation at all.* One needs only to know the factors g_R and the approximate values of the coefficients a_R. Some results obtained in this way—with the same assumptions as before in regard to values of the a's—are given in Table III (second column from the right). It will be seen that these are really quite good. The value of this method—and of the immediately preceding—lies in the fact that the calculated energy is not very sensitive to small changes in the coefficients, as long as these are of reasonable magnitudes.

Since Eq. (19) is rigorously true when the correct values of the a's are inserted, it gives a very valuable check upon the results obtained by other methods. For example, when the coefficients given by Sherman[13] (column 1a in Table III, page 491) for the 16 different types of structure of naphthalene are used, the resulting energy is $W=Q+4.0403\alpha$, in almost complete agreement with his value of $W=Q+4.0400\alpha$. Consequently one can be quite certain that there is no large error in his work. When the degree of the secular equation is reduced by equating coefficients arbitrarily, Eq. (19) is no longer necessarily exactly true. Thus, with Sherman's fifth degree coefficients (column 1b in Table III), the energy becomes $W=Q+4.0545\alpha$, which is different from the solution of the corresponding equation—$W=Q+4.0175\alpha$.

There is one final approximate method which is useful for order-of-magnitude calculations. Like the last, it does not require that the secular equation be set up at all, and, in addition, it does not require any knowledge of the factors g_R. If all unexcited structures are given the coefficient $c=1$, and all first excited structures the coefficient $c=\bar{c}$, then one can easily show that any equation of the set (14), for which R refers to an unexcited structure, can be expressed in the form

$$Q-W+[N(2-\bar{c})+B(\bar{c}-1)]\alpha=0. \tag{20}$$

Here B is defined as the number of interchanges in the molecule for which the corresponding exchange integral is equal to α—i.e., 6 for benzene, 11 for naphthalene, and so on. (The derivation of (20) assumes that all unexcited structures can be canonical simultaneously, and also that there are no "phantom orbitals," as in the case of the free radicals.[16]) The extreme variation of $\bar{c}$ seems to be approximately from 0.75 to 0.9 (this would give an upper and a lower limit to the energy), although it is possible that this limitation may not be valid in molecules widely different from those studied so far. If a rounded-off average value of $\bar{c}=5/6$ is used, Eq.

[16] Cf. L. Pauling and G. W. Wheland, J. Chem. Phys. 1, 362 (1933).

(20) becomes

$$W=Q+\tfrac{1}{6}(7N-B). \qquad (21)$$

The results of a number of calculations by this method are given in the last column of Table III. It will be seen that these are considerably better than one would have any right to expect.

States of Higher Multiplicity

The method of spin valence is especially advantageous in the treatment of systems of high multiplicity. The Slater method, of course, can also be extended to these cases, but, as far as the author is aware, no very convenient procedure for doing so has yet been described. The device of formally reducing the system to a singlet by the introduction of "phantom orbitals"[17] becomes very cumbersome as the multiplicity increases, and is hardly practicable except for doublet, and perhaps for triplet levels. The difficulty lies in the fact that this procedure does not allow the states under consideration to be separated from all those of lower multiplicity. The simplest possible example is the triplet level of the H_2 molecule. Here it is necessary to introduce two phantom orbitals, x and y, in addition to the real ones, a and b. There are then two structures,

$$\begin{matrix} a & b \\ | & | \\ y & x \end{matrix} \qquad\qquad a\text{—}b \qquad\qquad y\text{—}x,$$

which must be considered. (It is not legitimate to neglect the second, as would seem reasonable at first sight.) The secular equation is found in the usual way to be

$$\begin{vmatrix} Q-W-\frac{1}{2}\alpha & \frac{1}{2}(Q-W)+\frac{1}{2}\alpha \\ \frac{1}{2}(Q-W)+\frac{1}{2}\alpha & Q-W+\alpha \end{vmatrix}=0$$

or

$$W=Q+\alpha, \quad Q-\alpha.$$

Here, as before, Q is the coulomb integral, and α is the single exchange integral between a and b. All exchange integrals involving the phantom orbitals x and y vanish. Of the two roots, one corresponds to the singlet, and the other to the triplet level, but, before we can tell which is which, we have to calculate the singlet energy independently. This is found to be $W=Q+\alpha$, and consequently, the desired triplet energy is given by the second root, $W=Q-\alpha$. In the general case, the calculation can become quite complicated. In order to find the 20 quintet levels of an 8-electron problem, for example, we would have to solve a secular equation of the 132nd degree. Of the 132 roots thus obtained, 28 would correspond to the 14 singlet states (each occurring twice), 84 would correspond to the 28 triplet states (each occurring three times), and the remaining 20 would correspond to the desired quintet states.

A more straightforward application of the Slater method to such cases consists in actually setting up the proper number of independent wave functions, in the manner given by Kimball and Eyring,[6] and then evaluating the various matrix elements which occur in the secular equation. This latter is quite a laborious process, however, since no simple rules have yet been worked out for the states of higher multiplicity, analogous to those given by Kimball and Eyring[6] and by Pauling[17] for the singlet states.*

In contrast to the above, however, the method of spin valence is very simply applicable to systems of high multiplicity. The justification of the following procedure is quite straightforward, and will be left to the reader.[18] We introduce a *single* phantom orbital L, no matter what the multiplicity of the molecule may be, and to it we bond all the unshared electrons. (This apparent violation of the Pauli exclusion principle is legitimate here in consequence of the purely formal nature of the treatment.) Thus, for the triplet state of the H_2 molecule, we have the single structure

$$\begin{matrix} a & & b \\ & \searrow \quad \swarrow & \\ & L & \end{matrix}.$$

The corresponding function is

$$\Psi=\tfrac{1}{2}\sum_j(-1)^j P_j\{a(1)b(2)[\alpha(1)l_- -\beta(1)l_+] \times[\alpha(2)l_- -\beta(2)l_+]\},$$

where l_+ and l_- are constants, which are transformed under a rotation of axes in the same manner as α and β, respectively. The function Ψ is readily seen to be a linear combination of the three components of the triplet. There are only

[17] Cf. L. Pauling, J. Chem. Phys. **1**, 280 (1933); L. Pauling and G. W. Wheland, ibid. **1**, 362 (1933).

[18] Cf. M. Born, Ergebnisse d. Exakten Naturwiss. **1931**, 387.

* *Note added in proof:* Since the above was written, a method has been given by R. S. Bear and H. Eyring, J. Chem. Phys. **3**, 98 (1935).

TABLE IV.

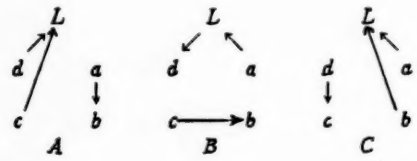
ϕ_i \ T_j	I	(ab)	(bc)	(cd)	(da)	Σ
A	A	$-A$	$A+B$	A	$C-B$	$A(Q-W)-(A+C)\alpha$
B	B	$B-A$	$-B$	$B-C$	B	$B(Q-W)+(A-2B+C)\alpha$
C	C	C	$C+B$	$-C$	$A-B$	$C(Q-W)-(A+C)\alpha$

two permutations to be considered, the identity I, and the single interchange (ab), both of which leave the structure unaltered. The secular equation is accordingly

$$|G_I+G_{(ab)}|=0 \quad \text{or} \quad |Q-W-\alpha|=0.$$

Thus the energy is simply $W=Q-\alpha$, in agreement with the result above.

A somewhat more complicated problem is that of the triplet states of cyclobutadiene. There are three structures to be considered



As before, a complete independent set of functions is obtained by arranging the orbitals in a circle and drawing all structures in which no two bonds intersect. The usual rules apply to the resolution of structures with crossed bonds, in terms of the canonical set. The functions are set up in a manner analogous to the one above for H_2. Corresponding to A, for example, we have

$$\Psi_A=\frac{1}{4(6)^{\frac{1}{2}}}\sum_j(-1)^jP_j\{a(1)b(2)c(3)d(4)\times[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\times[\alpha(3)l_--\beta(3)l_+][\alpha(4)l_--\beta(4)l_+]\}.$$

The calculation is given in Table IV.

The corresponding secular equation is

$$\begin{vmatrix} Q-W-\alpha & 0 & -\alpha \\ \alpha & Q-W-2\alpha & \alpha \\ -\alpha & 0 & Q-W-\alpha \end{vmatrix}=0.$$

The solutions are $W=Q$, $Q-2\alpha$, $Q-2\alpha$, in complete agreement with the results obtained by Hückel.[9]

As in the case of the singlet states, it would be possible to carry through a discussion of such matters as the reduction of the secular equation by taking advantage of the symmetry of the molecule, and the approximate methods of solving the secular equations. This would lead to nothing essentially new, however, and consequently need not be discussed here in any further detail.

ORBITAL DEGENERACY

The problem of orbital degeneracy can also be treated by the method of spin valence. As in the case of the Slater method, however, the treatment becomes too complicated to be of very much use, except in actual numerical calculations for quite simple systems. We can represent a general wave function as

$$\chi=\frac{1}{(2^N(2N)!)^{\frac{1}{2}}}\sum_i\sum_k\sum_j(-1)^ja_{ik}(P_ju_i)(P_j\varphi_k),$$

where the u_i's are functions of the spatial coordinates (analogous to the u of Eq. (3)), the a_{ik}'s are constants to be chosen so as to give the best possible function χ, and the other symbols have the same significance as before. Some simplification is afforded by the fact that whenever u_i assigns two electrons, say r and s, to the same orbital, then a_{ik} will vanish unless φ_k contains the factor $[\alpha(r)\beta(s)-\beta(r)\alpha(s)]$. If we apply perturbation theory by setting $(H-W)\chi=0$ and by then proceeding in the same manner as before, we obtain

$$\sum_i\sum_k\sum_j a_{ik}G_{ji}b_{kl}^{(j)}=0 \qquad (l=1, 2, \cdots p_N).$$

This set of simultaneous homogeneous linear equations for the a_{ik}'s takes the place of the set (9), and, like it, gives rise to a corresponding secular equation from which the energy can be obtained. It is doubtful if this method offers any advantages over the usual one, with which it is equivalent. It is given here only for the sake of completeness.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Structure of Cyanuric Triazide

Mr. E. W. Hughes has recently described a structure for cyanuric triazide,[1] which in general outline is similar to one which I found some time ago and which was briefly described by Sir William Bragg in *Nature* of last July.[2] It differs, however, from mine in certain important details. The atomic distances in the cyanuric ring are given as 1.33A and all equal, thus indicating an oscillating double bond as in benzene. I find two distances 1.38A and 1.31A, corresponding to fixed single and double bonds alternating in the ring. In Mr. Hughes' structure the azide group departs considerably from linearity, being bent 15° at the middle nitrogen atom, while in my structure the group is straight or very nearly so. In the azide group, the nitrogen atom, which is directly linked to the cyanuric ring is unfortunately not completely resolvable in the Fourier projection on the (0001) plane because of a similar nitrogen atom of the second molecule of the unit cell being separated from it in the plane of projection by only 0.92A, so that there is rather less precision in locating its center than is the case with the rest of the atoms. For this reason, it is not possible to be certain of the exact linearity of the azide group, but even so I estimate that any departure from it could not exceed 3° or 4°.

It is not possible to follow Mr. Hughes' work very closely, since he has not published the figures which he used for the intensities in his Fourier analysis nor the numerical values which he obtained from the summations, nor does he give any indication of the closeness of the points in the (0001) plane at which he carried out his summations.

I may point out, however, that Mr. Hughes' estimates of intensity were visual only. My intensity measurements were made on a Robinson photometer[3] and in my analysis I used the intensities from 99 planes of the (0001) zone, whereas Mr. Hughes only used 66 values. The intensities, which he has omitted are not in all cases the weakest. Many correspond to quite strong reflections, some of them having intensities which I found equal to one-half of the highest value I obtained for any plane in the zone. The Fourier series, which he used, must therefore be very far from convergent and it has been our experience in this laboratory that unless the series is very nearly convergent, that is, unless none but the very weakest reflections have been omitted, we do not obtain well-defined or correct positions for the atoms, nor do contour lines which follow faithfully the results of the calculations, these having been carried out at a sufficient number of points, appear smooth or circular round the atom centers.

My intensity measurements have recently been put on an absolute scale by a few accurate determinations using the ionization method and molybdenum rays, to eliminate absorption. This has revealed an interesting feature of the structure, namely, that the electron density at the centers of the atoms is unusually high, rising to above 8 and 10 electrons per square Angstrom unit for carbon and nitrogen, respectively. Now that the work is quite complete, I hope that it will soon be published in detail.

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February 8, 1935.

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[2] Bragg, Nature **134**, 138 (1934).
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Raman Spectra of Fused Salts

In order to assist in the interpretation of results obtained from a series of thermodynamic studies of fused salts, we have begun a search for Raman spectra in a number of salts in the fused condition.

We report some preliminary measurements of carefully purified salts made with a spectrograph of comparatively low dispersion. The mercury arc radiation was filtered with either an aqueous solution of sodium nitrite or a solution of iodine in carbon tetrachloride. No photochemical decomposition of the fused zinc chloride was observed after continued illumination using either filter. In the pure state these salts did not etch the Pyrex Raman cells even after being confined at over 500°C for several weeks. Exposure times varied from four to twenty-four hours.

The 100 cm^{-1} anti-Stokes line from the 4358A exciting line was not observed since it would lie too close to the 4339A mercury line for resolution. The 285 cm^{-1} frequency value is the least exact, only one comparatively poor plate being available for this frequency. The Stokes and anti-Stokes lines are of comparable intensity as might be expected for the temperature used.

Substance	Temperatures	Exciting line	Displaced frequencies (cm^{-1})
$ZnCl_2$	(400°, 430° and 500°C)	4358A	230±9; 98±5 (Stokes) 233±8 (anti-Stokes)
		4046A	285 (broad); 101±8 (Stokes) 231±5; 15±5 (anti-Stokes)
$ZnBr_2$	(440°C)	4358A	155±8; 79±10 (Stokes) 137±20 (anti-Stokes)

Krishnamurti[1] investigated the Raman spectra of a number of inorganic halides in the solid state at room temperature. Those substances with heteropolar binding showed no Raman spectra whereas homopolar substances such as the mercuric halides showed strong Raman lines. Zinc chloride and cadmium iodide, substances of intermediate polarity, whose crystal structure is of the layer lattice type showed weak Raman lines. Our data would classify zinc bromide in the intermediate group with zinc chloride and cadmium iodide, the higher electrical conductivity of the zinc bromide being offset by its lower melting point.

Krishnamurti[1] found a frequency shift for zinc chloride of 234 cm^{-1}, which is in satisfactory agreement with the higher frequency line found by us. The frequency shifts of 297 and 396 cm^{-1} found from concentrated aqueous solutions of zinc chloride by Hibben[2] are probably due to complex ions or molecules.[3, 4] Furthermore, Braune and Engelbrecht[5] have shown that the displaced frequencies of the mercuric halides are nearly the same for the fused salt as for the salt at room temperature. Grassman[6] and Thatte and Ganesan[7] obtained similar results for a number of nitrates. The fact that the Raman frequencies persist some hundred degrees above the melting point indicates that the frequencies found here are not due to vibrations in the crystal lattice but are rather due to oscillations in the zinc halide grouping.

The results for both zinc chloride and zinc bromide do not indicate a linear type of molecule. The determination of the angle between the valence bonds and strength of bonds awaits additional data.

We failed to observe Raman lines from fused LiBr, $PbCl_2$, $PbBr_2$ and $CdCl_2$, but the experimental conditions for obtaining these lines were not as satisfactory as with the zinc salts.

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February, 27, 1935.

[1] Krishnamurti, Ind. J. Phys. **5**, 113 (1930).
[2] Hibben, Proc. Nat. Acad. Sci. **18**, 532 (1932).
[3] Damaschun, Zeits. f. physik. Chemie **B16**, 92 (1932).
[4] Braune and Engelbrecht, Zeits. f. physik. Chemie **B11**, 416 (1931).
[5] Braune and Engelbrecht, Zeits. f. physik. Chemie **B19**, 303 (1932).
[6] Grassman, Zeits. f. Physik **77**, 616 (1932).
[7] Thatte and Ganesan, Ind. J. Phys. **8**, 341 (1934).

The Absolute Rate of a Chemical Reaction

Various writers[1, 2, 3] have attempted to formulate the factors determining the absolute rate of a chemical reaction. To a first approximation the task is not difficult. There are two methods of approach. One method is to calculate the number of favorable collisions from kinetic theory. The other is to treat the colliding molecule as a complex and apply the laws of statistical mechanics and chemical equilibrium for what they are worth. The two methods correspond at every point. Thus, the heat of activation in the latter treatment becomes the factor which determines the number of collisions of sufficient violence in the former method. The collision radius in the kinetic theory determines the moment of inertia and rotational entropy of the complex in the thermodynamic treatment. The greater the entropy of the complex, the greater must be the probability of reaction. By an arbitrary choice of collision radii, the "steric" factor may often be made unity, but this does not really give us any more information than we had before. Both methods involve uncertainties due to the lack of exact knowledge of force constants, collision radii, etc.

Recently Eyring[4] has proposed to treat the subject by a method which is essentially the second method mentioned above. His method is not, therefore, novel, nor does it produce any results new to statistical mechanics. What he does propose that is new is to calculate the contours of the potential surface by wave mechanics so that the various uncertainties mentioned above may disappear. It may even be possible to calculate the rate of reflection at a barrier. This latter quantity may be described as a true steric factor.

One may await results to see how well it will succeed. Presumably no one would claim that it is now possible to calculate the energy of any but the simplest chemical bonds with any precision by wave mechanics. Certainly a survey of the amount of work required to reach a satisfactory value for the heat of dissociation of the hydrogen molecule does not inspire one with confidence. The method of Heitler and London may be a better approximation in the case of a reactive complex than a stable molecule; it would be very fortunate if this is the case. It is, of course, possible to adapt calculations to experimental data, but in doing this one may produce agreement by changing one factor when some other factor is really at fault.

Nevertheless, the writer has believed for a long time that it should be possible to determine all the constants of a reaction rate from measurements at a single temperature.

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February 27, 1935.

[1] W. H. Rodebush, J. Am. Chem. Soc. **45**, 606 (1923); J. Chem. Phys. **1**, 440 (1933).
[2] M. Polanyi and E. Wigner, Zeits. f. physik. Chemie (Haber band), 439 (1928).
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The Raman Spectrum of Deuterium

A number of observers have studied the emission spectra of mixtures of hydrogen and deuterium. The Fulcher bands for HD and D_2 have been photographed.[1] In the extreme ultraviolet Jeppesen,[2] and Beutler and Mie,[3] have obtained emission spectra from hydrogen-deuterium mixtures and have ascribed several bands to HD. From these data on HD, Urey and Teal[4] have calculated molecular constants for the molecule D_2 in the ground state. No experimental data for this molecule in this state appear to have been obtained.

We have obtained Raman spectra of gaseous deuterium (99.5 percent D_2) at a pressure of 2.5 atmos., using Hg 2537 as an exciting line. 24- to 48-hour exposures were made. Two rotation lines and the Q branch of the vibration line were obtained. Their frequencies and mean deviations from

TABLE I. *Observed and calculated Raman frequencies of D_2.*

v	J	ν obs. cm^{-1}	ν calc. cm^{-1}	Difference	I calc.
0→0	0→2	179.6±0.5	179.1	0.5	
	1→3	298.3±1.3	297.4	0.9	
0→1	0→0	2989.5±1.3	2996.7	−7.2	0.00*
	1→1		2994.7	−5.2	0.90
	2→2		2991.2	−1.7	1.21
	3→3		2986.2	3.3	0.33
	4→4		2974.7	14.8	0.26

means in measuring plates are given in Table I, together with frequencies calculated from the equation of Urey and Teal, for the rotation-vibration energy levels of the molecule in the ground state. Using a formula given by Placzek[5] and due to Mannenbeck, we have calculated the relative intensities I of four of the strongest lines in the vibrational Q branch. The result gives 2990.0 cm^{-1} for the position of the center of gravity of the Q branch, and this is in agreement with the observed frequency.

The constants of Urey and Teal are therefore confirmed. This result is important in connection with the use of deuterium to establish the structure of hydrogen-containing molecules.[6] In such cases $M-D$ distances are assumed equal to $M-H$ distances, where M is any atom. The greatest deviation from this assumption would probably occur in D_2; and since no deviation is found in this case the assumption appears to be justified. Moreover the force constant for D_2 is the same as that for H_2, and this suggests that $M-D$ force constants are equal to those for $M-H$.

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DON M. YOST

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March 2, 1935.

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[5] G. Placzek, *Rayleigh-Streuung und Raman-Effekt* (Leipzig, 1934) Eqs. (15), (15a), p. 343.
[6] F. Rasetti reports a line ν_{16}^{00} for hydrogen. Phys. Rev. **34**, 367, (1929). The matter is worth further investigation.
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A Transition in Potassium Superoxide

During the study of the magnetic properties[1] of potassium superoxide, KO_2, I noticed that on cooling in liquid air the substance changes from a deep orange to a light cream color. In order to see whether or not this change in color accompanies a transition from one form to another, and if so to determine the transition temperature, the following experiments were carried out.

Samples of the superoxide and of sodium chloride were put in a glass tube 7 mm in diameter, each in a layer 2 cm deep, with the two junctions of a differential thermocouple at the centers of the two layers, and the junction of another thermocouple (for measuring the temperature) at the center of one of the layers. The tube was sealed from the atmosphere by a plug of cotton followed by a layer of picien. The tube was enclosed in a copper jacket about 5 mm thick, in order to insure a uniform heat transfer between the cell constants and the surroundings. Mercury was added as a further aid to this end and the whole was enclosed in a test tube. The thermocouples were single junction and were made of No. 32 copper and constantan wire joined with silver solder. The differential thermocouple was connected directly to a Leeds and Northrup Type R galvanometer which had a period of 5.5 sec. and a sensitivity of 2.7 mm/m per mv. The galvanometer scale was 60 cm from the instrument. No damping resistance was found necessary with this instrument. This differential thermocouple was used only as a means of observing differences of temperature between the oxide and the chloride. The actual temperature of the oxide was measured by means of the other thermocouple which was used in conjunction with a Leeds and Northrup Type K potentiometer. This thermocouple was calibrated by comparison with nine fixed points.

Warming curves were obtained from liquid air temperature to the temperature of melting ice. The cell was first cooled in liquid air for about an hour, the air was then removed from the enclosing Dewar flask, a cotton plug was inserted into the mouth of the flask to prevent irregular heating due to convection, and the cell was allowed to rise to room temperature. The most uniform curves were obtained when the time of warming over the temperature range studied was between 4 and 5 hours.

Cooling curves were obtained by enclosing the cell in an unsilvered Dewar flask and cooling by immersing this flask in liquid air. The flask that was used allowed the temperature of the cell to fall from room temperature to liquid air temperature in about 4 hours.

The warming curves and cooling curves all showed a pronounced break, corresponding to a transition at the temperature $-75.5°\pm0.5°$C. (No break in this region was shown by control curves obtained by replacing the superoxide in the cell by sodium chloride.) Observation of the color change showed that it occurs at the same temperature, to within about $\pm15°$.

The experimental method is not sufficiently delicate to distinguish between a true polymorphic transition and a gradual transition;[2] if the transition is of the latter type, it is reasonably sharp, extending over a temperature range not greater than three or four degrees.

The normal superoxide ion is in the state $^2\Pi$, and the separation of the two levels $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ is probably about the same as for NO, 121 cm^{-1}. It is interesting to note that this energy value is equal to kT at the temperature $T=213°$A, only 15° from the observed transition temperature; though until more definite evidence is obtained the suggestion that the transition of the solid substance is related to the electronic transition of the molecules must be considered as speculative.

The author is grateful to Professor Linus Pauling for his interest in the investigation.

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[1] E. W. Neuman, J. Chem. Phys. **2**, 31 (1934).
[2] Linus Pauling, Phys. Rev. **36**, 430 (1930).
[3] Now at Carroll College, Capitol Hill, Helena, Montana.